

QUINOXALINE POLYMERS AND COPOLYMERS DERIVED FROM
1,4-BIS(1'-NAPHTHALENYLOXALYL)BENZENE

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AVCO SYSTEMS DIVISION

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16. Abstract <p>A route for the synthesis of a new monomer, 1,4-bis[(1'-naphthalenyl)-oxalyl]benzene, was devised, and six polymers and copolymers were prepared from this monomer, 1,4-bis(phenyloxalyl)benzene, 3,3'-diaminobenzidine and 3,3',4,4'-tetraaminobenzophenone. Thermogravimetric analysis showed that decomposition of these quinoxaline polymers and copolymers sets in at about 500°C but does not become significant in an inert atmosphere below 600°C. Oxidation becomes significant at about 550°C and the phenylquinoxaline homopolymer is somewhat more oxidation resistant than is the 1-naphthalenyl-quinoxaline homopolymer. The inherent viscosity of most of the polymers and copolymers were in the range 1.9 - 3.0 dl/g which indicates that they had high molecular weights. Stress-relaxation measurements showed that, with two exceptions, the homopolymers and copolymers exhibited two second-order transition temperatures, one at about 204.4°C (400°F) and the other at about 315.6°C (600°F). No gross differences in the high temperature plasticity was observed between the naphthalenyl- and the phenyl-quinoxaline homopolymers. Work was begun on a method for cross-linking polyquinoxalines. A new monomer, p-(methyloxalyl)benzil, was synthesized, and model reaction studies showed that cross-linking of 2-methylquinoxaline polymers by a Michael condensation with dimaleimides will probably occur.</p>					
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FOREWORD

This report presents the work accomplished by AVCO Corporation during the period of May 9, 1973 to June 30, 1974 on NASA Contract NAS 3-16802 "Synthesis of Improved Polyphenylquinoxalines". The work was administered by the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, with Mr. Peter Delvigs as Project Manager.

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I. INTRODUCTION

A. Background

As an outgrowth of aerospace developments of the past decade, strong interest has arisen in quinoxaline polymers as matrix materials for composites employing filaments, such as boron, graphite and silicon carbide, which have notably high specific strength and stiffness. Because some polyquinoxaline resins have attractive high temperature properties, they make possible the extension of the temperature range of utilization of the composites further toward the ultimate capability of the reinforcement. Polyquinoxalines having aromatic ring substituents have, therefore, joined the ranks of the new, heterocyclic polymers such as the polyimides, the polybenzimidazoles, the polybenzoxazoles, the polybenzothiazoles and the pyrrones.

Early research in polyquinoxalines was performed by Stille and co-workers¹⁻³ and by de Gaudemaris and co-workers⁴⁻⁶ who prepared polyquinoxalines from the condensation of various bis-(1,2-aryldiamines) and several di(arylglyoxals). Work on polyphenylquinoxalines was performed by Wrasidlo and Augl⁷⁻¹² and by Hergenrother, Levine and co-workers¹³⁻¹⁹.

The work on the polyphenylquinoxalines showed that polymers with high glass transition temperatures (in the order of 250 - 435°C) and high decomposition temperatures (in the order of 510 - 560°C) were obtainable. The oxidative resistance in air, as measured by weight loss in thermogravimetric analysis experiments or by isothermal aging at 371°C, was notable; introduction of oxygen linkages into the molecule, however, gave greater oxidative susceptibility in some polymers. On the other hand, the thermoplasticity of the polyphenylquinoxalines above their glass transition temperatures limits the range of their use for structural applications. Furthermore, some polyphenylquinoxalines form highly viscous solutions which wet reinforcing filaments with difficulty. These deficiencies affect adversely the use of these polymers in the preparation of laminates.

Further research on polyquinoxalines was, therefore, directed toward decreasing their high temperature plasticity and toward improving their solubility characteristics. Polymers with decreased plasticity have been sought through ladder polymers and through incorporation of substituents which permit cross-linking of polymer chains after the initial fabrication with the polyquinoxaline has been accomplished. Novel methods for polyquinoxalines were also explored as an answer to the fabrication problem. Among the investigations on ladder polymers may be mentioned the work of Stille and co-workers²⁰⁻²⁵, Marvel and co-workers²⁶⁻³⁰, Jackson and Schroeder³¹, Russo³², Arnold and Van Deusen³³ and

Naarmann³⁴. Among the approaches for introducing cross-linking sites may be noted the work of Wentworth and Mulligan³⁵ and Augl, Duffy and Wentworth³⁶ who demonstrated that poly-p-tolylquinoxalines could be cross-linked by heating in an argon atmosphere. Hergenrother³⁷ accomplished cross-linking by introducing p-cyanophenoxyphenyl substituents on the quinoxaline ring in modified polyphenylquinoxalines and heating in an inert atmosphere after fabrication with the linear polymer had been accomplished. Presumably, the cyano-group trimerized to form sym-triazine rings. Cross-linking in this manner raised the glass transition temperature by 50°C. Among the novel approaches used to aid processibility is the method of Serafini, Delvigs and Vannucci³⁸ who accomplished polymerization in situ from 35% solutions of each of the two monomers and thus avoided the impregnation problems otherwise encountered from high-viscosity high-molecular weight polyphenylquinoxaline solutions.

An approach to a simultaneous solution of the processing problems due to high viscosity polymer solutions and to thermoplasticity at high temperature has been investigated in condensation polymers other than the polyquinoxalines. The method entails the incorporation into the polymer of bulky, planar groups standing crosswise to the polymer chain. Thus, Morgan^{39,40} prepared aromatic polyesters from bisphenols in which the phenylene rings were joined by bulky, planar groups derived from phenolphthalein and related compounds or were structures such as diphenylmethylenes, 1-indanylidene, 9-fluorenylidene, 9-xanthenylidene and the like. Such structures imparted marked increases in the glass transition temperature and enhanced the solubility in low boiling solvents. Similar approaches were taken by Vinogradova and Korshak⁴¹.

B. Purpose and Scope of Present Work

The present work is concerned with the preparation and preliminary evaluation of quinoxaline polymers and copolymers having improved processing characteristics and low plasticity at high temperature when compared with polyphenylquinoxalines previously synthesized. Two methods to achieve these goals were investigated: (1) to raise the glass transition temperature of the polymer by the introduction of a planar, bulky pendant group into the linear polymer chain and (2) to prepare a linear polyquinoxaline capable of being cross-linked and, subsequently, to cross-link this polymer. In the course of such work, the synthesis and characterization of new monomers, the study of model reactions and the preparation, characterization and physical evaluation of new polymers and copolymers were undertaken.

The polymers and copolymers containing the planar, bulky groups were prepared from 3,3'-diaminobenzidine by reaction with 1,4-bis-(phenyloxalyl)benzene and 1,4-bis[(1'-naphthalenyl)oxalyl]benzene, a new monomer. The preparation of a polymer having latent cross-linking capability entailed the preparation of a new monomer, p-(methyl-oxalyl)benzil, use of the monomer to prepare a polyquinoxaline containing a reactive methyl group and subsequently cross-linking by reacting the methyl group in a Michael condensation with a bis-maleimide. Details of the reaction used to prepare the monomers and polymers are given in Section III, "Experimental Results".

Polymer specimens for evaluation were prepared by casting films from solutions of the polymers and copolymers. Methods used to characterize the monomers and as proof of structure included determination of melting points, elemental analysis, infrared spectrophotometric analysis, nuclear magnetic resonance spectrophotometry and gas chromatographic analysis. The characterization and evaluation of the polyquinoxalines comprised determination of the inherent viscosity, the elemental composition, the glass transition temperature, the solubility in selected solvents, the isothermal weight loss in air in long-term exposure at elevated temperatures, the tensile properties at elevated temperatures and the time-to-rupture and weight loss under tensile loading at elevated temperatures and the performance of infrared spectrophotometric analysis and of thermogravimetric analysis in air and helium. Details of the methods of characterization and evaluation are presented in Section III.

II. SUMMARY

A route for the synthesis of a new monomer, 1,4-bis[(1'-naphthalenyl)oxalyl]benzene, was devised, and six polymers and copolymers were prepared from this monomer, 1,4-bis(phenyloxalyl)benzene, 3,3'-diaminobenzidine and 3,3',4,4'-tetraaminobenzophenone. It was found that polymerization of 1,4-bis[(1'-naphthalenyl)oxalyl]benzene and tetraamines occurred more readily at elevated temperatures and that the viscosities of solutions of the polymers and copolymers were low enough to permit ready preparation of cast films.

1,4-Bis[(1'-naphthalenyl)oxalyl]benzene and the intermediate used in its synthesis, 1,4-bis[(1'-naphthalenyl)acetyl]benzene, were characterized and their structures were established by derivative preparation and elemental and infrared spectrophotometric analysis. The polymers and copolymers were characterized and evaluated by elemental, infrared spectrophotometric and thermogravimetric analysis, by the determination of their inherent viscosity, second-order transition temperature, isothermal weight loss at 315.6°C (600°F) and 371.1°C (700°F), solubility in selected solvents, and their tensile properties and by the time at which these materials ruptured under sustained loading at elevated temperatures. The thermogravimetric analysis showed that decomposition of the quinoxaline polymers and copolymers sets in at about 500°C but does not become significant in an inert atmosphere below 600°C. Oxidation becomes significant at about 550°C and the phenyl-quinoxaline homopolymer is somewhat more oxidation resistant than is the 1-naphthalenyl-quinoxaline homopolymer. The inherent viscosities of most of the polymers and copolymers were in the range 1.9 - 3.0 dl/g which indicates that they had high molecular weights. Stress-relaxation measurements showed that, with two exceptions, the homopolymers and copolymers exhibited two second-order transition temperatures, one at about 204.4°C (400°F) and the other at about 315.6°C (600°F). No gross differences in the high temperature plasticity was observed between the naphthalenyl- and the phenyl-quinoxaline homopolymers. The naphthalenyl-quinoxaline homopolymer was soluble in N-methylpyrrolidone and the phenyl-quinoxaline homopolymer insoluble. Both homopolymers were soluble in o-dichlorobenzene, chloroform, sym-tetrachloroethane and m-cresol. Both homopolymers had about the same tensile strength whereas the tensile strength of the copolymers was slightly lower.

Work was begun on a method for cross-linking polyquinoxalines. A new monomer, p-(methyloxalyl)benzil, was synthesized and the structure of this compound and of an intermediate required for its preparation, p-(phenylacetyl)phenylacetone, were established by derivative preparation and elemental, infrared spectrophotometric and nuclear magnetic resonance analysis. Model reaction studies showed that cross-linking of 2-methyl-quinoxaline polymers by a Michael condensation with dimaleimides will probably occur.

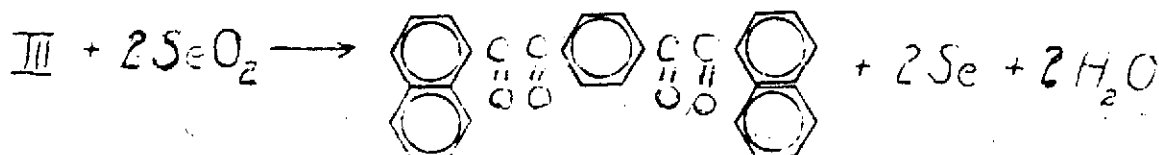
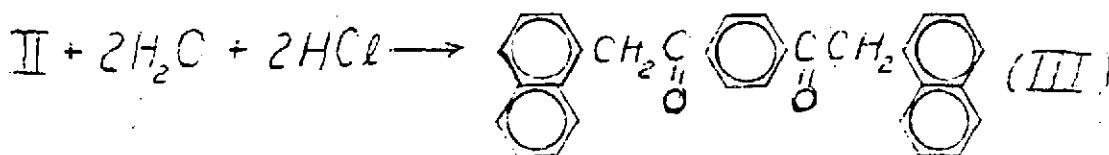
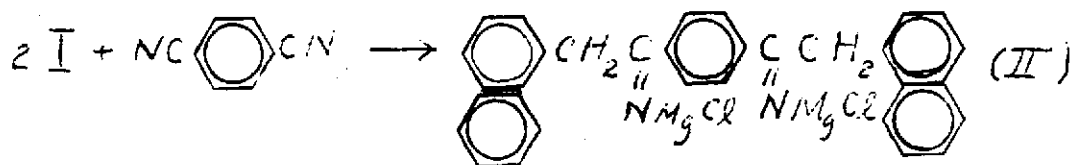
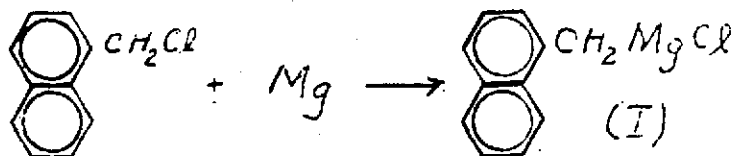
III. EXPERIMENTAL RESULTS

Included in the Experimental Results are: (A) Monomer Preparation and Characterization (B) Preparation of Polymers and Copolymers (C) Characterization of Polymers and Copolymers.

A. Monomer Preparation and Characterization

1. 1,4-Bis[(1'-naphthalenyl)oxalyl]benzene

This compound was synthesized in four steps from 1-chloromethylnaphthalene but without isolation of 1-naphthalenylmethylmagnesium chloride or of the bis-ketimine:



a. Synthesis and Characterization of 1,4-Bis[(1'-naphthalenyl)-acetyl]benzene

1-Naphthalenylmethylmagnesium chloride was prepared in 86.7% yield from 88.3 g (0.5 mole) 1-chloromethylnaphthalene in ethyl ether in accordance with the procedure of Grummitt and Buck⁴². The solvent was distilled off and was replaced with 250 ml toluene. Powdered 1,4-dicyanobenzene, 27.3 g (0.21 mole) was added. An exothermic reaction set in, the green-yellow solution became orange and a precipitate formed. The mixture was refluxed for two hours, cooled and poured into 250 g ice and 100 g concentrated hydrochloric acid. The mixture was stirred mechanically and 500 ml chloroform and 250 ml water were added. The mixture was filtered yielding 58 g (67% crude yield) of impure 1,4-bis[(1'-naphthalenyl)-acetyl]benzene melting at 192 - 200°C. Additional quantities of the crude product were obtained from the filtrate as follows. The phases in the filtrate were separated, the aqueous phase was extracted with 25 ml chloroform and the chloroform extract was combined with the organic phase. The combined organic phases were extracted with three 250 ml portions of water and dried over anhydrous calcium chloride. The calcium chloride was filtered off, the solution was cooled to -10°C and 11 g of crude 1,4-bis[(1'-naphthalenyl)acetyl]benzene (m.p. 191 - 8°C) was recovered by filtration. The chloroform filtrate was evaporated to dryness, and the residue was recrystallized from toluene yielding 2.6 g of product. The total crude yield based on 1,4-dicyanobenzene was thus 71.6 g (82.7%). In a second preparation, the crude yield was 100% and the purified yield was 60%.

Purification of the crude compound was accomplished by two crystallizations from refluxing toluene (17.5 ml/g) with activated charcoal decolorization (1 g "Norit"/37 g compound). 1,4-Bis[(1'-naphthalenyl)acetyl]benzene so obtained melted at 206 - 7°C. A specimen for elemental and infrared spectrophotometric analysis was obtained by a third crystallization from dioxane (6.4 g/250 ml); the analytical sample melted at 205 - 6.5°C. Elemental analysis (F & M Model 185 Carbon Hydrogen and Nitrogen Analyzer) showed 86.02% carbon, 5.45% hydrogen (theoretical values, 86.93 and 5.35% respectively). Figure 1 is the infrared spectrum of 1,4-bis[(1'-naphthalenyl)acetyl]benzene. The absorption band at 2900 cm^{-1} is consistent with the presence of the $-\text{CH}_2-$ or of the $-\text{CH}_2-\text{C}-$ group, the strong bands at 1685 and 1215 cm^{-1} are

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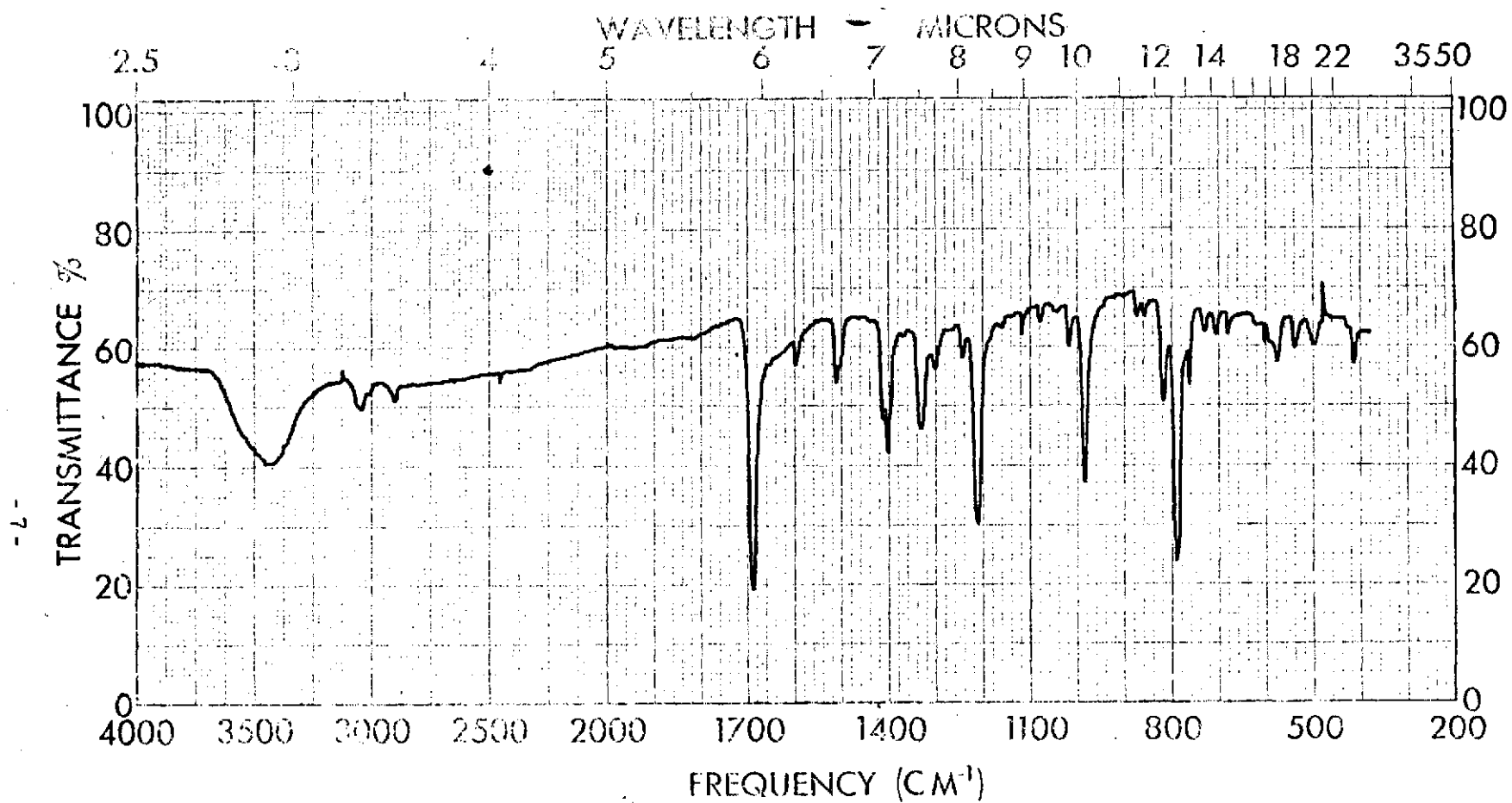


Figure 1. Infrared Spectrum of 1,4-Bis[(1'-naphthalenyl)acetyl]benzene.

consistent with aromatic ketones, the bands at 3040, 1600, 1510, 1400, 790 and 760 have been associated with 1-naphthalenyl derivatives, and the bands at 3050, 1600, 1510, 1210, 1120 - 1020 and 820 cm^{-1} , have been attributed to para-substituted benzene⁴³. The absorptions are thus consistent with the structure 1,4-bis[(1'-naphthalenyl)acetyl]benzene.

The bis(2,4-dinitrophenylhydrazone) of 1,4-bis[(1'-naphthalenyl)acetyl]benzene was prepared by treating a solution of 0.5 g of 1,4-bis[(1'-naphthalenyl)acetyl]benzene in 20 ml hot dioxane with a hot solution of 2,4-dinitrophenylhydrazine (prepared by dissolving 0.82 g 2,4-dinitrophenylhydrazine in 4 ml concentrated H_2SO_4 , adding 6 ml water, and diluting with 10 ml absolute ethanol). A bright orange precipitate formed, the mixture was heated for 15 minutes and filtered hot. The crude bis(2,4-dinitrophenylhydrazone) was recrystallized once from dioxane. The purified material melted sharply with decomposition at 245°C and was subjected to an elemental analysis: found - 64.90% carbon, 4.82% hydrogen, 13.38% nitrogen; theory - 65.11% carbon, 3.90% hydrogen, 14.46% nitrogen. Figure 2 is the infrared spectrum of the bis(2,4-dinitrophenylhydrazone). The absorption at 1685 cm^{-1} seen in Figure 1 and characteristic of $\text{C}=\text{O}$ is no longer present in Figure 2. A new set of bands at 1590 and 1615 cm^{-1} , which may be due to >C=N- or to >C=NNH- or to conjugated NO_2 is present. The strong bands at 1500, 1520 and 1320 are probably due to the aryl nitro structure⁴³.

An alternate procedure for preparing 1,4-bis[(1'-naphthalenyl)acetyl]benzene by the reaction of bis[(1'-naphthalenyl)methyl]cadmium and terephthaloyl chloride was unsuccessful. Experimental details are given in Appendix 1. The synthesis of the isomer, 1,4-bis[(1'-naphthalenyl)carbonyl]phenylenedimethylene by the Friedel-Crafts reaction between naphthalene and terephthaloyl chloride was also unsuccessful (Appendix 2).

b. Synthesis and Characterization of 1,4'-Bis[(1'-naphthalenyl)oxalyl]benzene

A mixture of 20.7 g (0.05 mole) 1,4-bis[(1'-naphthalenyl)acetyl]benzene (m.p. $206 - 7^\circ\text{C}$) and 200 ml dioxane was heated to effect solution and 11.3 g (0.102 mole) selenium dioxide was added. The mixture was stirred mechanically and refluxed for 17 hours and was then filtered hot yielding a filtrate and a residue. When the hot dioxane filtrate cooled, bright yellow crystals of crude 1,4-bis[(1'-naphthalenyl)oxalyl]benzene deposited which when filtered off and dried weighed 1.0 g and

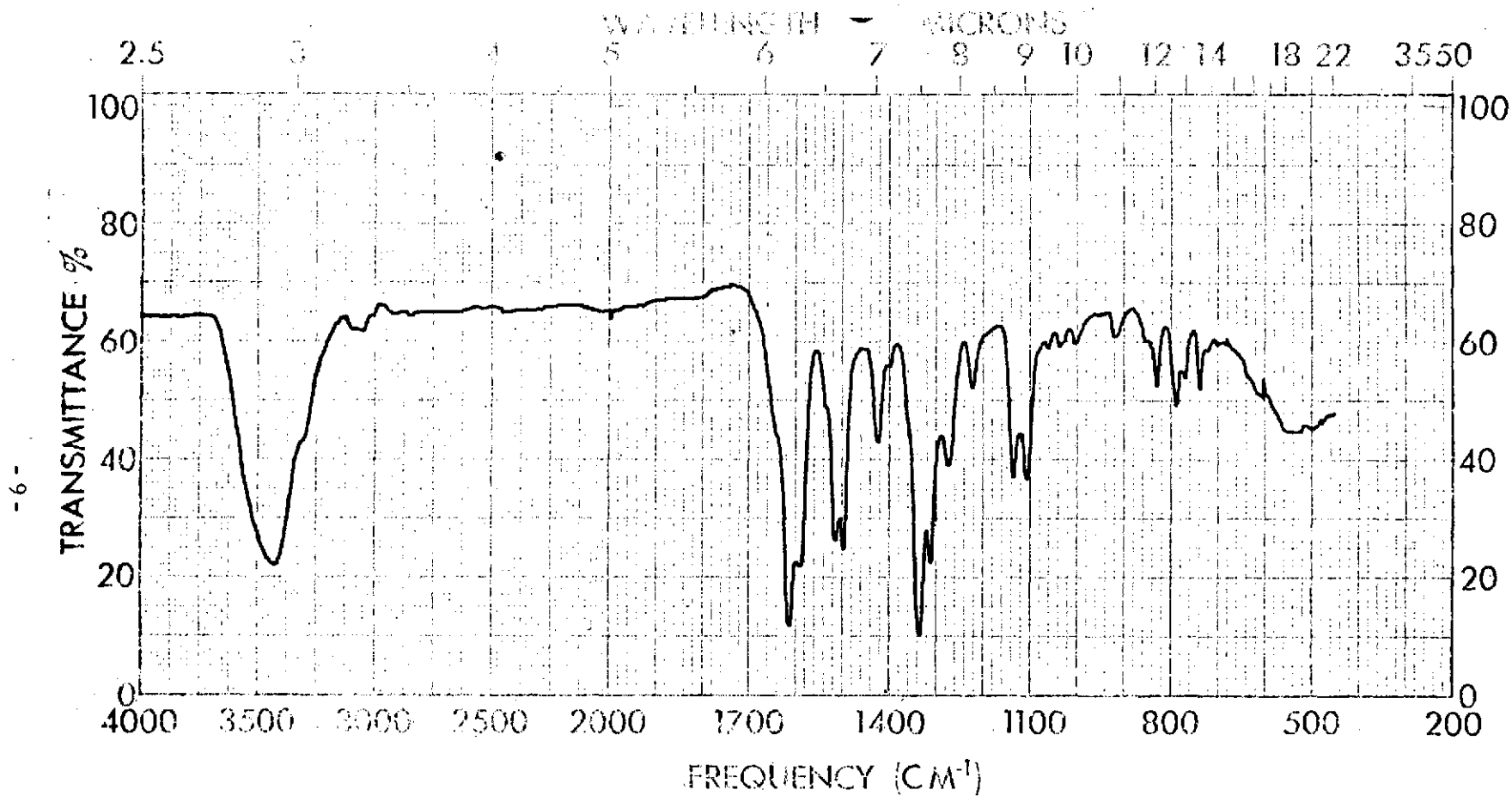


Figure 2. Infrared Spectrum of 1,4-Bis(1'-naphthalenylacetyl)benzene-bis(2'',4''-dinitrophenylhydrazone).

melted at 264 - 71°C; additional fractions weighing 3.0 g were obtained by concentrating the dioxane filtrate. Crude 1,4-bis[(1'-naphthalenyl)oxalyl]benzene was also recovered from the residue which was placed into two Soxhlet extractors and extracted with 150 ml dioxane in each extractor. The extracts were cooled and filtered yielding 10.9 g crude product m. p. 264 - 71°C. A second set of extractions and work-up gave 2.4 g, m. p. 256 - 68°C. Evaporation of the dioxane filtrates gave 2.0 g crude for a total crude yield of 19.3 g or 87.3% of theory. In a second preparation, the crude yield was 79.5% based on 1,4-bis[(1'-naphthalenyl)acetyl]benzene. (The yield of purified product, on the same basis, was 70.8%.)

When 6.9 g of the crude compound was recrystallized from 70 ml of dimethylformamide, 6.5 g 1,4-bis[(1'-naphthalenyl)oxalyl]benzene, melting at 270 - 2°C, was obtained. An elemental analysis of the compound showed 81.97% carbon and 3.32% hydrogen; the theoretical values are 81.44% and 4.10% respectively.

Figure 3 is the infrared spectrum of 1,4-bis[(1'-naphthalenyl)oxalyl]benzene and may be compared with Figure 1. Absorption at 2900 cm^{-1} present in Figure 1 and associated with methylene is absent in Figure 3 which is consistent with oxidation of $-\text{CH}_2-$ to $\text{C}=\text{O}$. In Figure 3, as contrasted to Figure 1, the absorption due to carbonyl is twinned; two bands are present in the 1600 - 1700 cm^{-1} region at 1650 and 1685 cm^{-1} (cf at 1685 cm^{-1} in Figure 1) and two bands are present in the 1150 to 1250 cm^{-1} region at 1180 and 1215 cm^{-1} (cf at 1215 cm^{-1} in Figure 1). This is consistent⁴³ with the presence of two different aryl ketone types in 1,4-bis[(1'-naphthalenyl)oxalyl]benzene:



The bands associated with para-substituted benzene and with 1-naphthalenyl are present in Figure 3 with some slight shifting compared with Figure 1. These observations are consistent with the assignment of the structure of 1,4-bis[(1'-naphthalenyl)oxalyl]benzene to the new compound. Unexpectedly many bands

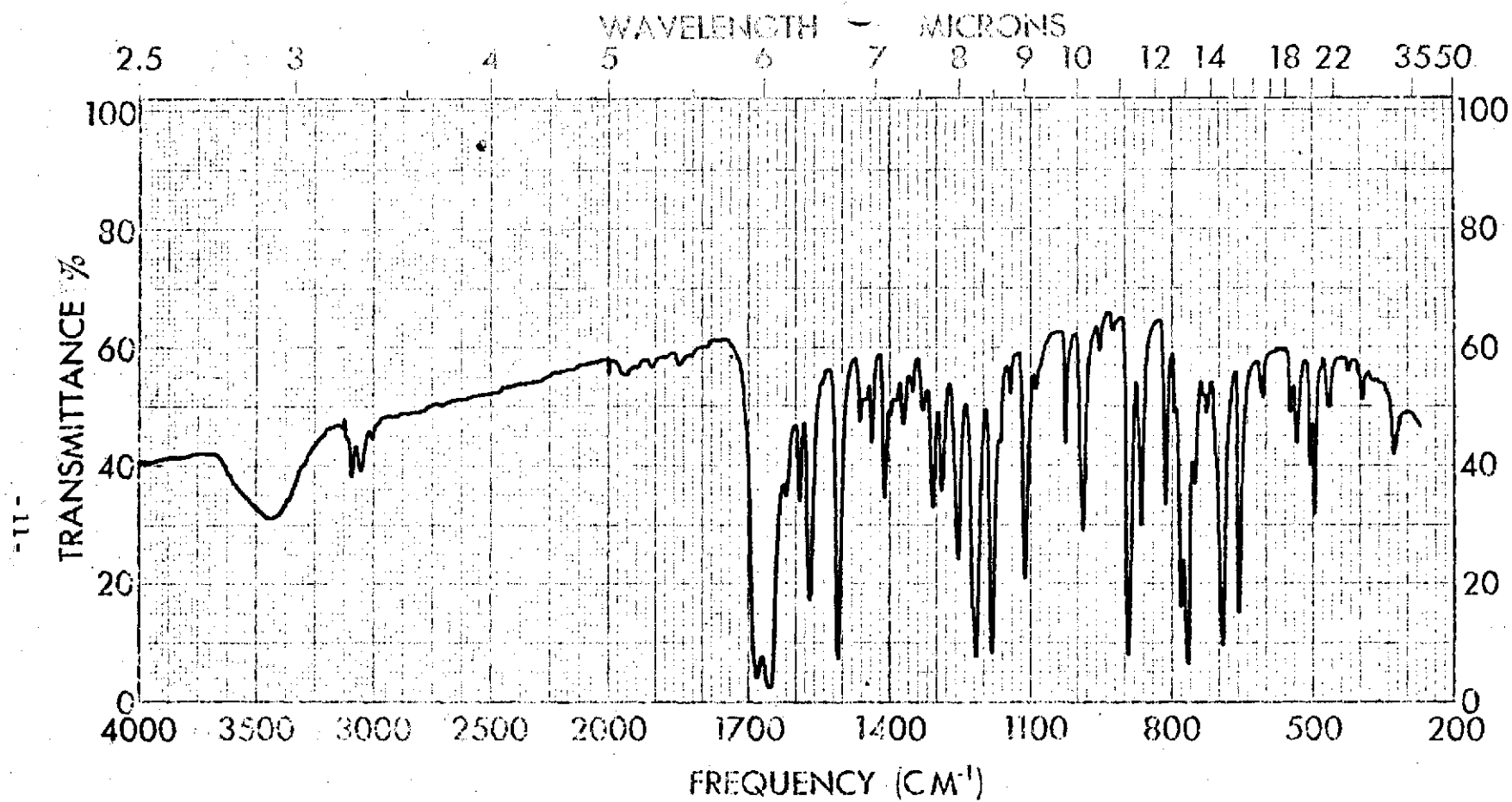


Figure 3. Infrared Spectrum of 1,4-Bis[(1'-naphthalenyl)oxalyl]benzene.

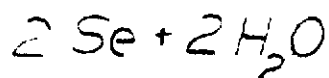
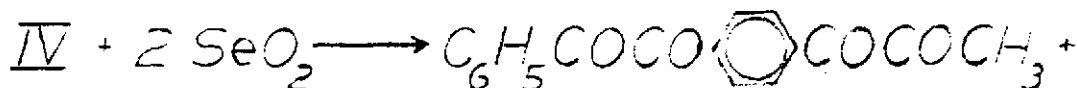
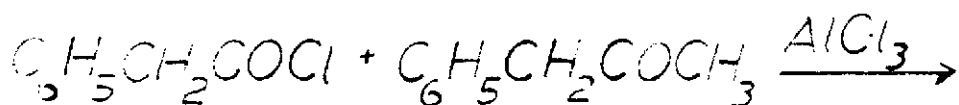
not present in Figure 1 are found in Figure 3 (at 3100, 1650, 1620, 1570, 1460, 1440, 1370, 1290, 1180, 890, 860, 660 and 500 cm^{-1}). Some changes in relative intensities were also noted (at 1510, 1330, 1300 cm^{-1}).

As a further mode of establishing the identity of the compound as 1,4-bis[(1'-naphthalenyl)acetyl]benzene, another derivative, i.e., 1,4-bis[3'-(1''-naphthalenyl)quinoxal-2'-yl]-benzene, was prepared. o-Phenylenediamine (from Eastman Kodak) was recrystallized from 4 parts of water with "Norit" decolorization under a blanket of nitrogen and dried under vacuum; the product melted at 101-3°C. A mixture of 2.2 g (0.005 mole) 1,4-bis[(1'-naphthalenyl)oxalyl]benzene in 25 ml dimethylformamide heated to 149°C was treated with 2.2 g (0.02 mole, 100% excess) o-phenylenediamine dissolved in 25 ml dimethylformamide (dropwise addition in 5 minutes). The solution was stirred mechanically and refluxed for 3 hours. The product crystallized out when the solution was allowed to cool to room temperature. The crystals were filtered off, washed successively with dimethylformamide and acetone and dried. The yield was 1.7 g m.p. 302-304°C. Elemental analysis of the compound showed 85.86% carbon, 4.16% hydrogen and 9.69% nitrogen (theoretical values for 1,4-bis[3'-(1''-naphthalenyl)quinoxal-2'-yl]benzene are 85.98, 4.47 and 9.55% respectively).

The infrared spectrum of the derivative is shown in Figure 4.

2. p-(Methyloxalyl)benzil

This compound was prepared in two steps including the synthesis of p-(phenylacetyl)phenylacetone and its oxidation to p-(methyloxalyl)benzil:



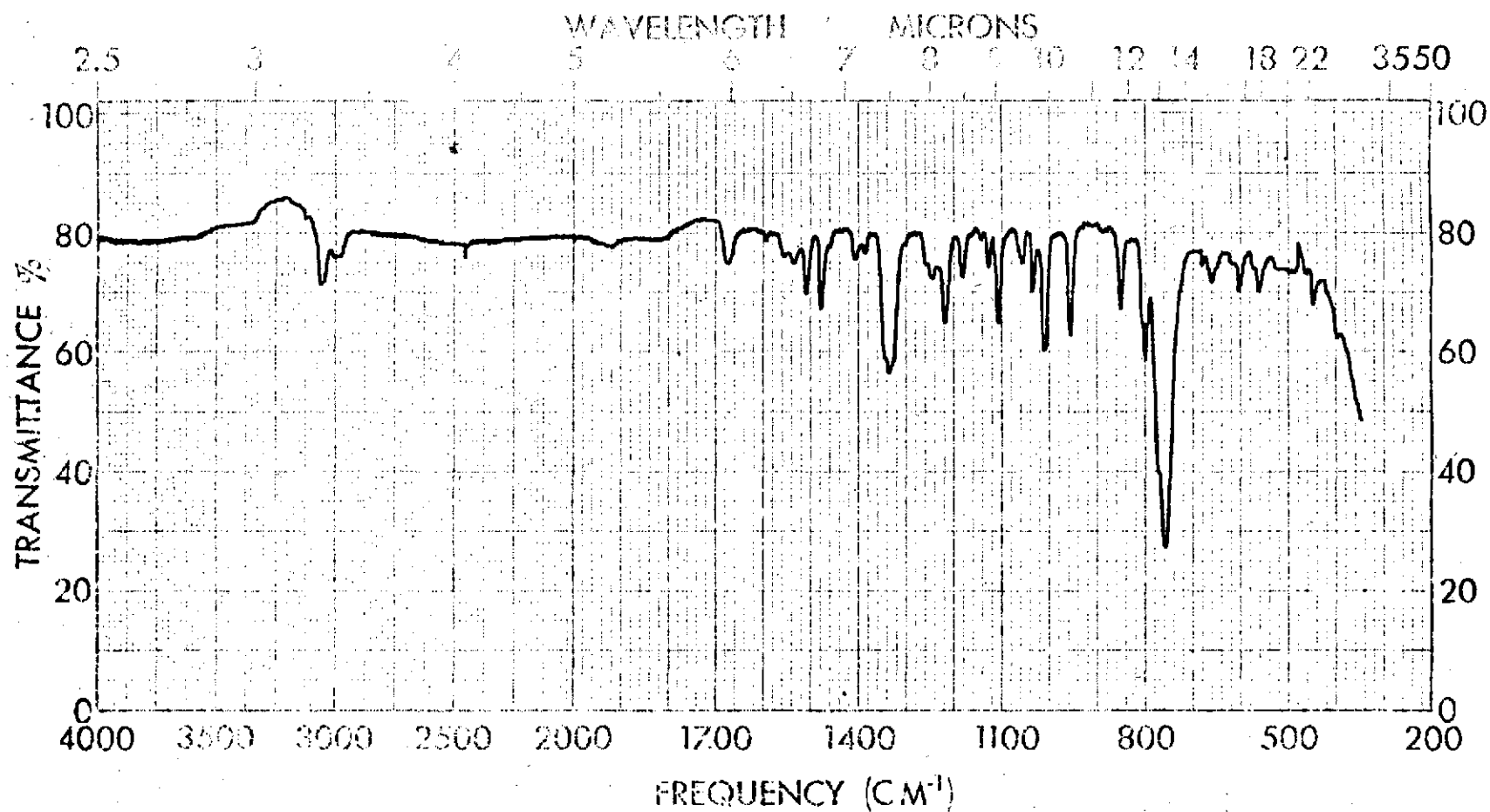


Figure 4. Infrared Spectrum of 1,4-Bis[3'-(1''-naphthalenyl)quinoxal-2'-yl]benzene.

a. Synthesis and Characterization of p-(Phenylacetyl)phenyl-
acetone

Phenylacetone (73.3 g, 0.53 mole) was added dropwise to a mechanically stirred slurry of 155.5 g (1.17 mole) aluminum chloride in 250 g carbon disulfide. A solution of 83.6 g (0.53 mole) phenylacetyl chloride in 50 ml carbon disulfide was added dropwise to the stirred aluminum chloride complex. After the initial evolution of hydrogen chloride had diminished in rate, the mixture was refluxed for 1 1/2 hours and then cooled. (Absorption and titration of the hydrogen chloride evolved showed that at least 85% of the phenylacetyl chloride had reacted.) The resulting two phases were separated by siphoning off the top (CS₂) layer which was discarded. The bottom layer was poured into 300 g concentrated hydrochloric acid and 700 g crushed ice. The two phases which formed were separated and the bottom (aqueous) phase was extracted with one 100-ml and with one 150-ml portions of chloroform. The extracts were combined with the upper (organic) layer, and the resulting solution was extracted with 3 250-ml portions of water. The solution was dried over anhydrous calcium chloride and the chloroform was distilled off. The residue was distilled at low pressure (50 - 100 μ). The fractions which were obtained are shown in Table I. Distillation was halted because decomposition of the pot residue set in. The pot residue was discarded.

TABLE I
DISTILLATION OF REACTION MIXTURE OF PHENYLACETONE AND
PHENYLACETYL CHLORIDE

Fraction No.	Boiling Point °C	Yield g	Comment
1	46-48	31	Recovered phenylacetone
2	50-180	2.7	
3	180-187	2.1	Crystallized during distillation
4	187-194	9.4	Solid
5	202-205	9.0	Viscous liquid

Fraction 4 was recrystallized from 50 ml ethanol, and a solid (1206-135-7) weighing 1.5 g and melting at 104 - 105.5°C was recovered. Concentration of the filtrate gave a second crop of crystals (0.3 g yield) which melted sharply at 106°C.

By means of nuclear magnetic resonance (NMR) and infrared (IR) spectro-photometry, it was now shown that this compound is p-(phenylacetyl)phenylacetone. Figure 5 is its NMR spectrogram and shows a methyl group at $\delta = 2.1$ and methylene groups at $\delta = 3.7$ and $\delta = 4.25$. Since there is no splitting in these resonance peaks, they are isolated from one another. This is consistent with



where, as can be seen, the two methylenes are isolated from one another and from the methyl group. The two methylene groups in p-(phenylacetyl)phenylacetone differ from one another in that one is α to a benzoyl group and the other to an acetyl group. It is, therefore, consistent with the assignment of this structure to 1206-135-7 that its NMR spectrum should show two methylene groups. The region $\delta = 7$ through $\delta = 8$ shows resonance which is due to para-substituted benzene which is again consistent with the assigned structure. Finally, the integration of the proton peaks (8.5:2:2:3) is consistent with p-(phenylacetyl)phenylacetone.

Figure 6, the infrared spectrum of 1206-135-7, shows absorption at frequencies which are characteristic of chemical structural units which are present in p-(phenylacetyl)phenylacetone. According to Rao⁴⁴ aryl ketones absorb at 1700 to 1680 and 1275 to 1025 cm^{-1} and alkyl ketones at 1725 to 1705 and 1325 to 1215 cm^{-1} . Compound 1206-135-7 absorbs in the aryl ketone region at 1680 cm^{-1} and at 1010, 1060, 1110, 1160, and 1230 cm^{-1} (most prominent among others) and in the alkyl ketone region at 1720 and 1230, 1320 and 1340 cm^{-1} . Absorption characteristic of the acetyl group is associated with sets of bands at 2950 to 2850, at 2925 to 3010 cm^{-1} , at about 1425 and at about 1360 cm^{-1} ; in 1206-135-7 absorption is found at 2880, 2930, and 3000 cm^{-1} , at 1430, 1420, and 1360 cm^{-1} . Absorption characteristic of the phenacyl group is associated with sets of bands at about 750 and 695 cm^{-1} ; in 1206-135-7, these are found at 735 and 695 cm^{-1} .

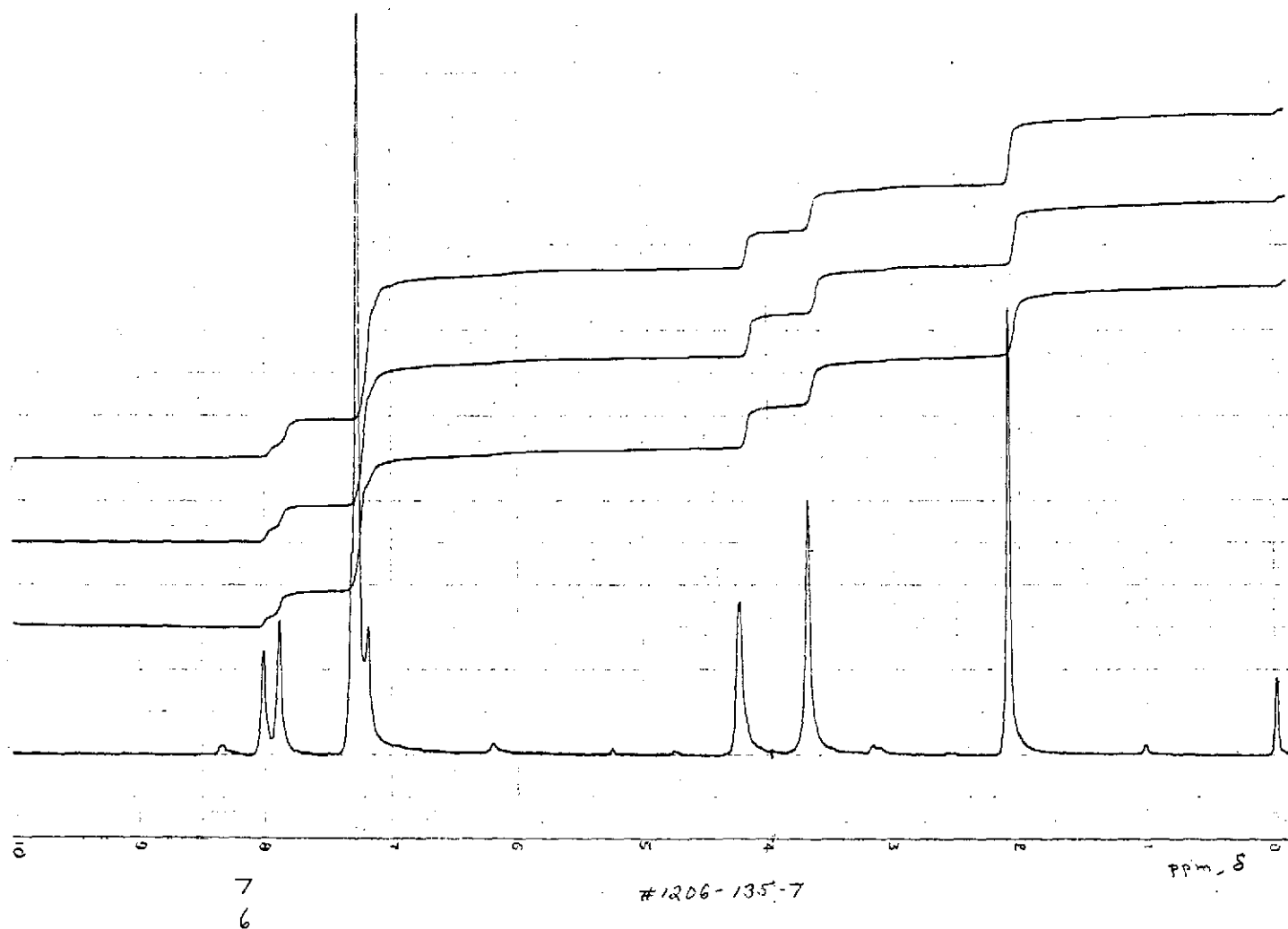


Figure 5. Nuclear Magnetic Resonance Spectrum of Compound 1206-135-7
[p-(Phenylacetyl)phenylacetone] in Deuterated Chloroform.

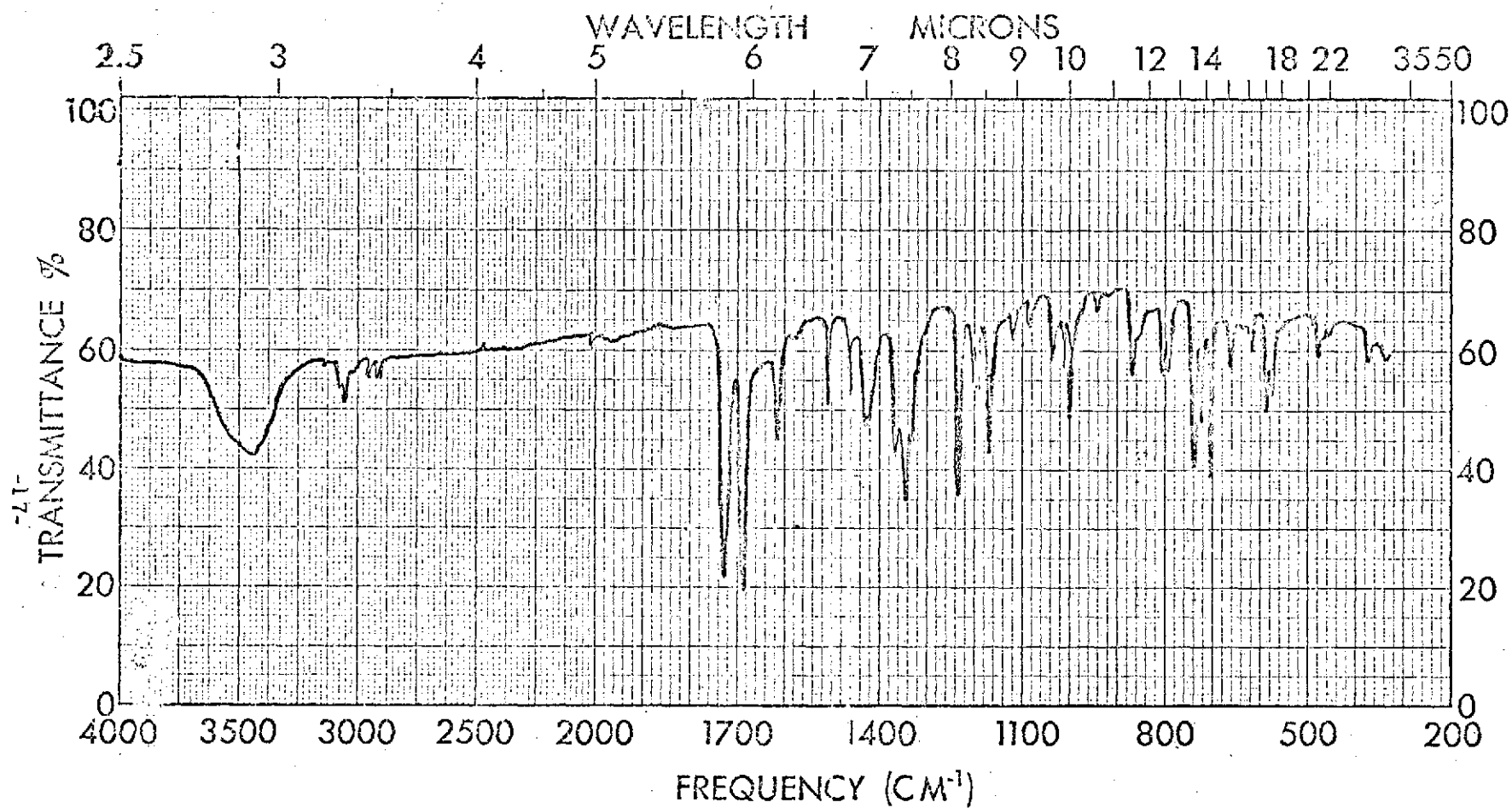


Figure 6. Infrared Spectrum of Compound 1206-135-7 [p-(Phenylacetyl)phenylacetone].

The identity of 1206-135-7 having thus been established as p-(phenylacetyl)phenylacetone, the concentration of this compound in the complex Friedel-Crafts reaction mixture was then sought in order to determine the yield. Gas chromatography was employed for this purpose; a 12 foot x 0.25 inch stainless steel column packed with SE-30 on diatomaceous earth and held isothermally at 250°C, an injection port temperature of 225°C and a thermal conductivity detector held at 285°C were used. The elution time for 1206-135-7 (Figure 7) was established as 15 minutes and a relationship was calculated between the found peak height and the known concentration of 1206-135-7 in the solution injected into the chromatographic apparatus. The yield of p-(phenylacetyl)phenylacetone was then sought in the crude fraction (boiling at 90 - 212°C at 50 - 100 μ) obtained in a repeat preparation (details follow) by injecting a solution of this crude fraction into the chromatographic apparatus. The chromatogram of the crude fraction is shown in Figure 8. From the peak height at 15 minutes, and the known concentration of the fraction, it was calculated that a maximum of 3.9% of p-(phenylacetyl)phenylacetone was present. Since the crude fraction represented 45.9% of the total reaction mixture, the yield of p-(phenylacetyl)phenylacetone was established as a maximum of 1.79%.

In the repeat preparation, the possibility of a consecutive reaction of phenylacetyl chloride with p-(phenylacetyl)phenylacetone, was considered and therefore a large excess of phenylacetone was used in order to reduce the extent of this undesired reaction. Phenylacetone (670.9 g, 5 moles) was added during a one-hour period to a stirred mixture of 881.7 g (6.61 moles) anhydrous aluminum chloride and 500 ml carbon disulfide. The slurry was heated to 43°C while 154.6 g (1 mole) of phenylacetyl chloride was added with mechanical stirring during one hour while the temperature dropped to 33°C. (Absorption and titration of the hydrogen chloride evolved showed that at least 94% of the phenylacetyl chloride had reacted.) The mixture was allowed to stand overnight and was poured into a mixture of 2.43 kg concentrated hydrochloric acid and 6 kg crushed ice. The acid phase was extracted with 3 250-ml portions of chloroform which were combined with the organic phase. The organic phase was then extracted with 2 1-liter portions of water and then was distilled in vacuo to remove the chloroform. Phenylacetone was then distilled off from 100°C to 109°C at 17 mm. A third fraction (1206-140-3) weighing 114.9 g was taken between 90°C and 212°C at 50 - 100 μ , and a fourth fraction weighing 34.9 g was taken at 209 - 280°C at 10 - 80 μ . The residue weighed 100.5 g.

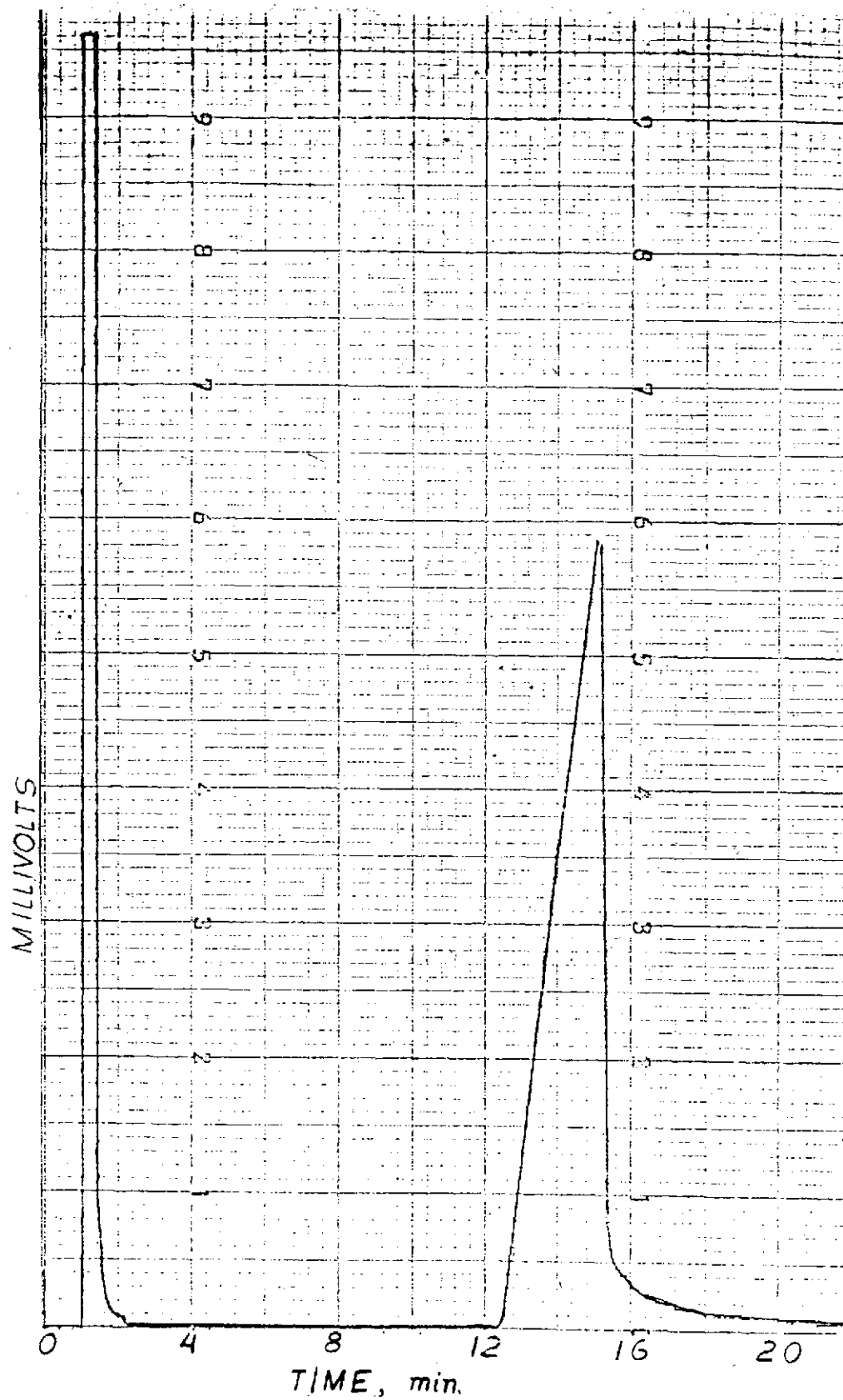


Figure 7. Gas Chromatogram of Compound 1206-135-7
[p-(Phenylacetyl)phenylacetone].

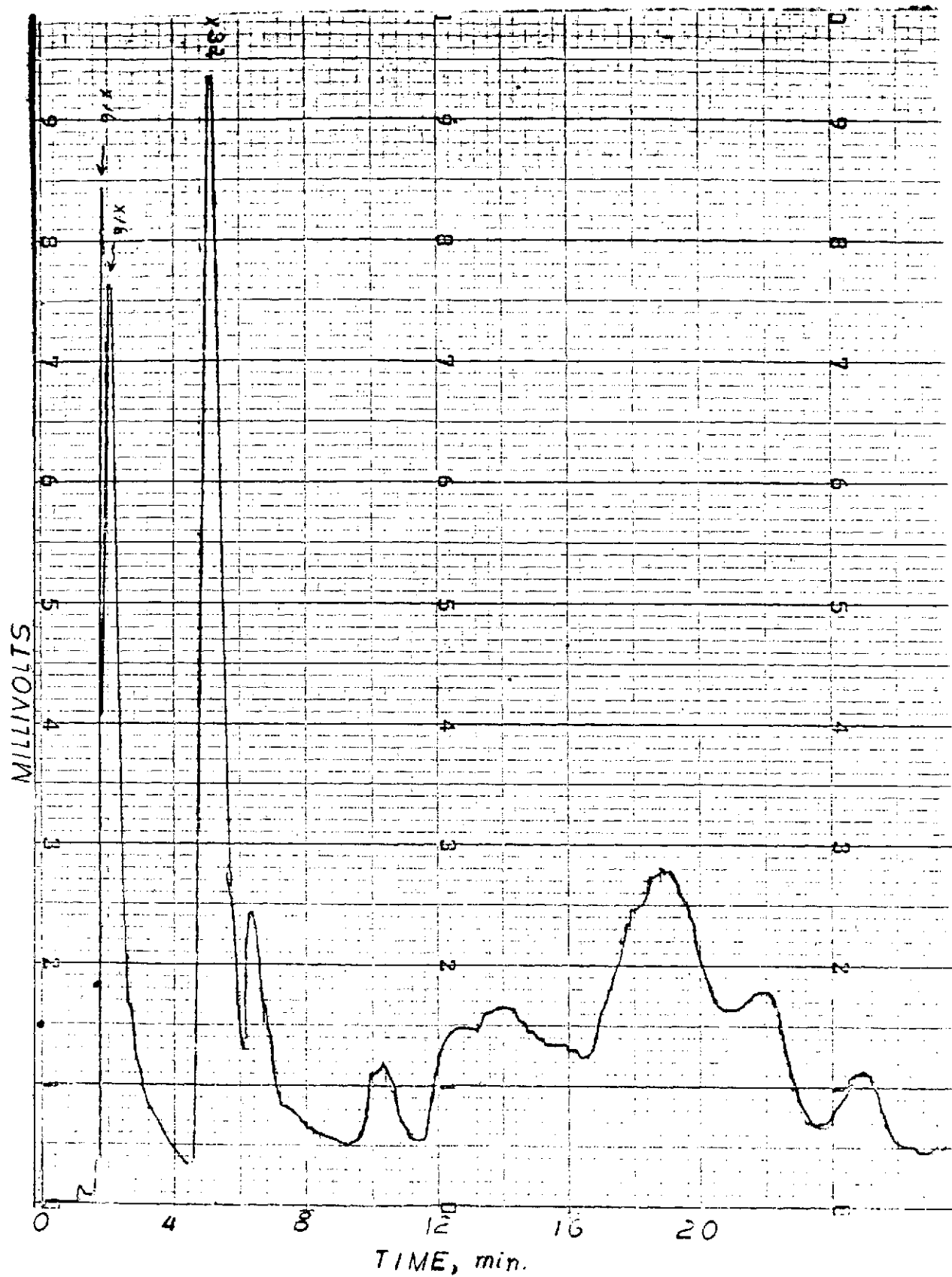


Figure 8. Gas Chromatogram of Crude Fraction Boiling at 90 - 212°C at 50 - 100 μ .

To obtain a supply of p-(phenylacetyl)phenylacetone, 1206-140-3 was re-distilled and the fractions listed in Table II were obtained. Fraction 1206-146-6, a mixture of white platelets and a liquid phase, was filtered and the residue (1206-146-7) was washed with 5 ml carbon tetrachloride. Compound 1206-146-10, weighing 0.8 g and melting at 105 - 106°C, was thus obtained. The same technique was used on the combined fractions 1206-146-4 and -5 and 0.8 g of compound 1206-152-6 melting at 105 - 6°C was obtained. Because 1206-146-10 and 1206-152-6 had the same melting point as 1206-135-7, they were considered to be p-(phenylacetyl)phenylacetone.

b. Oxidation of p-(Phenylacetyl)phenylacetone and Characterization of p-(Methyloxalyl)benzil

A mixture of 1.6 g (6.35×10^{-3} mole) p-(phenylacetyl)phenylacetone, 1.4 g (12.6×10^{-3} mole) selenium dioxide and 20 ml dioxane was refluxed for 4 1/2 hours. The mixture was filtered to remove the selenium which was washed with a few ml dioxane. The dioxane filtrate and washings were combined and distilled off under low pressure. The residue was extracted with 20 ml boiling isopropyl ether. An oil (1206-151-5) separated, and the isopropyl ether was decanted hot and cooled in a CO₂ / propanol bath. Yellow crystals formed (1206-153-1) which were filtered off and dried. These were obtained in 0.2 g yield and they melted at 65 - 78°C. 1206-153-1 was extracted with boiling hexane, the hot solvent was decanted from an oil which separated and the hexane was allowed to cool. Yellow crystals melting at 83 - 86°C (1206-153-3) were obtained. A second extractive crystallization gave crystals 1206-153-9 melting at 87 - 89°C. Evidence that 1206-153-3 and 1206-153-9 are p-(methyloxalyl)benzil was obtained by NMR and IR spectrophotometry. The infrared spectrum of 1206-153-3 is shown in Figure 9 (reduced slave copy). The spectrum shows the presence of α -diketone because of absorption at 1715 cm⁻¹ (Colthup tables give absorption at 1710 - 1730 cm⁻¹); aryl α -diketone (Ar CO CO Ar) because of absorption at 1672 cm⁻¹ (reported at 1680 cm⁻¹); aryl ketone is evidenced because of absorption at 1210 cm⁻¹. The presence of a C-acetyl group is shown by the absorption at 3100 and 3060 cm⁻¹ and at 1352 cm⁻¹ and the masked shoulder 1420 cm⁻¹ (better seen in a section of the full-scale spectrum Figure 10). Finally, the absorption at 865 cm⁻¹ is indicative of p-substitution.

TABLE II

DISTILLATION OF A CRUDE FRACTION OBTAINED
IN THE SYNTHESIS OF p-(PHENYLACETYL)PHENYLACETONE

Fraction No.	Boiling Point °C	Pressure μ	Yield g
1206-144-3	41-120	5-10	11
-4	125-130	7-10	11.8
-5	125-133	10	19.3
-6	126-131	10-15	5.5
-7	140-150	10	2.7
-8	153-162	10-15	3.5
1206-146-1	163-167	15	4.8
-2	175-190	15	3.1
-3	168-180	15	10.7
-4	172-183	15	9.6
-5	172-182	15	4.5
-6	175-177	20	11.2
-7	174-179	20	4.7

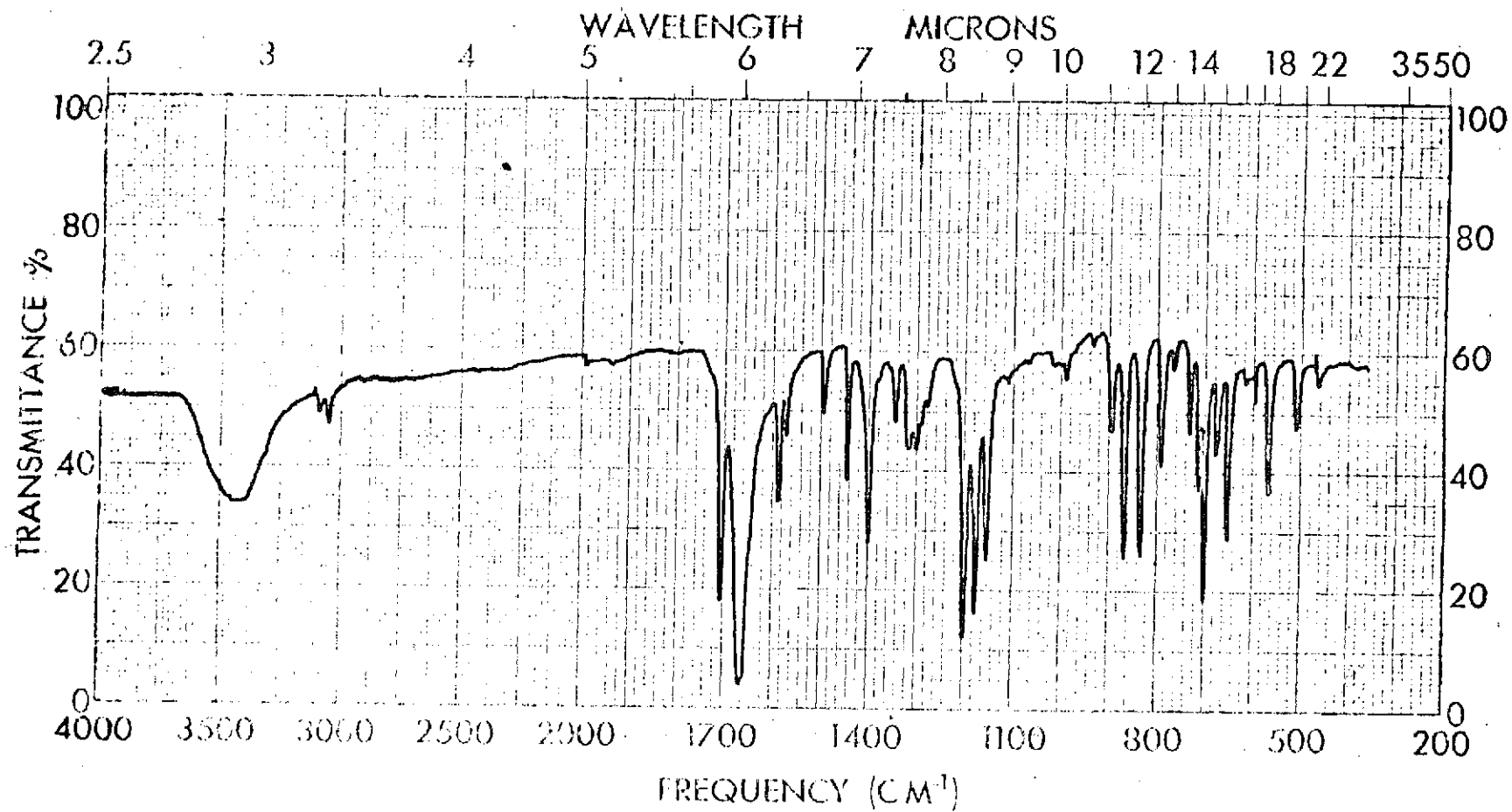


Figure 9. Infrared Spectrum of Compound 1206-153-3 [p-(Methyloxalyl)benzil].

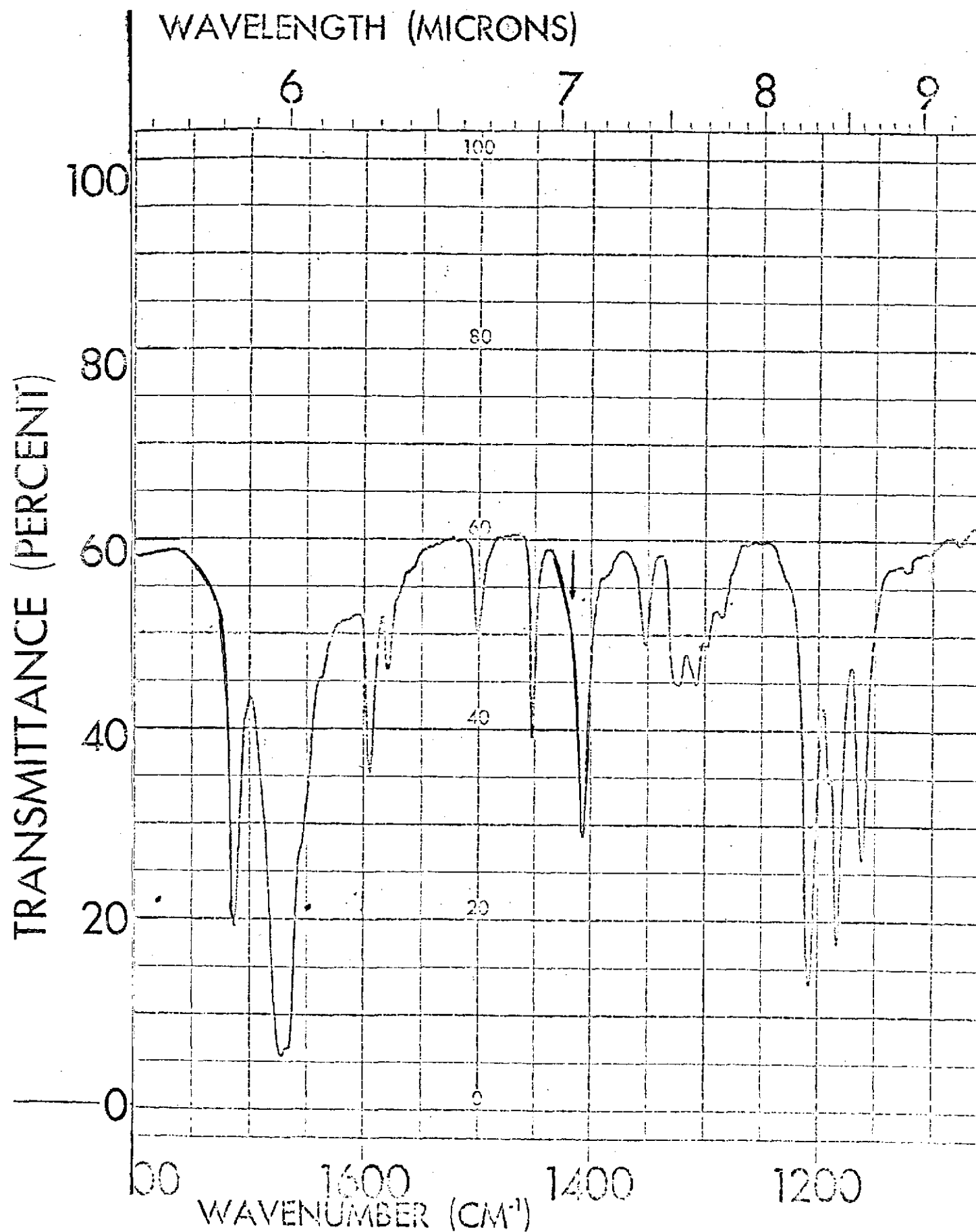


Figure 10. Portion of Full-Scale Infrared Spectrum of Compound 1206-153-3.

The NMR spectrophotometric evidence (Figure 11) that p-(methyloxalyl)benzil had been produced was obtained by using the combined samples 1206-153-3 and 1206-153-9 (1206-153-10) since the individual samples were insufficient for the test. Figure 11 shows the presence of an isolated methyl group (singlet at $\delta = 2.5$) and substituted aromatic groups in the region $\delta = 7.4$ to $\delta = 8.2$. Significantly, the two peaks due to methylene seen in Figure 5 are absent in Figure 11 which is consistent with oxidation of methylene to carbonyl. The resonance visible in the region $\delta = 0.8$ to 1.2 may be due to an impurity part of which is also observable in the carbon tetrachloride solvent. A temperature programmed gas chromatographic analysis of 1206-153-10 (Figure 12) showed that an impurity is present which elutes at 257.5°C and that p-(methyloxalyl)benzil elutes at $262 - 4^{\circ}\text{C}$. From the peak height it was estimated that 1206-153-10 is 89% pure. An isothermal gas chromatographic separation at 250°C of 1206-153-10 showed elution occurred in 14 minutes. The infrared spectrum (Figure 13) of p-(methyloxalyl)benzil obtained by trapping the compound as it eluted from the column (and which is therefore highly pure) differs little from 1206-153-3. No absorption peaks are missing which might give some clue as to the nature of the impurity.

Appendix 3 gives the details on attempted, but unsuccessful, methods for preparing p-(methyloxalyl)benzil. These included (1) selenium dioxide oxidation of p-phenacylpropiophenone which gave, instead, p-propionylbenzil, (2) nitrosation of p-phenacylpropiophenone to 1-p-(1'-phenyl-1'-oxo-2'oximino-ethyl)phenyl-1,2-propanedione-2-oxime and the unsuccessful hydrolysis of the latter, (3) nitrosation of p-propionylbenzil to p-(2-oximinopropionyl)benzil and the unsuccessful hydrolysis of the latter.

c. Model Reaction for Crosslinking through the Michael Condensation

In order to provide evidence concerning the possibility that cross-linking could be achieved by a Michael condensation between polyquinoxalines derived from p-(methyloxalyl)benzil and p-phenylenedimaleimide, the reaction between 2-methyl-3-phenylquinoxaline and N-phenylmaleimide was attempted:

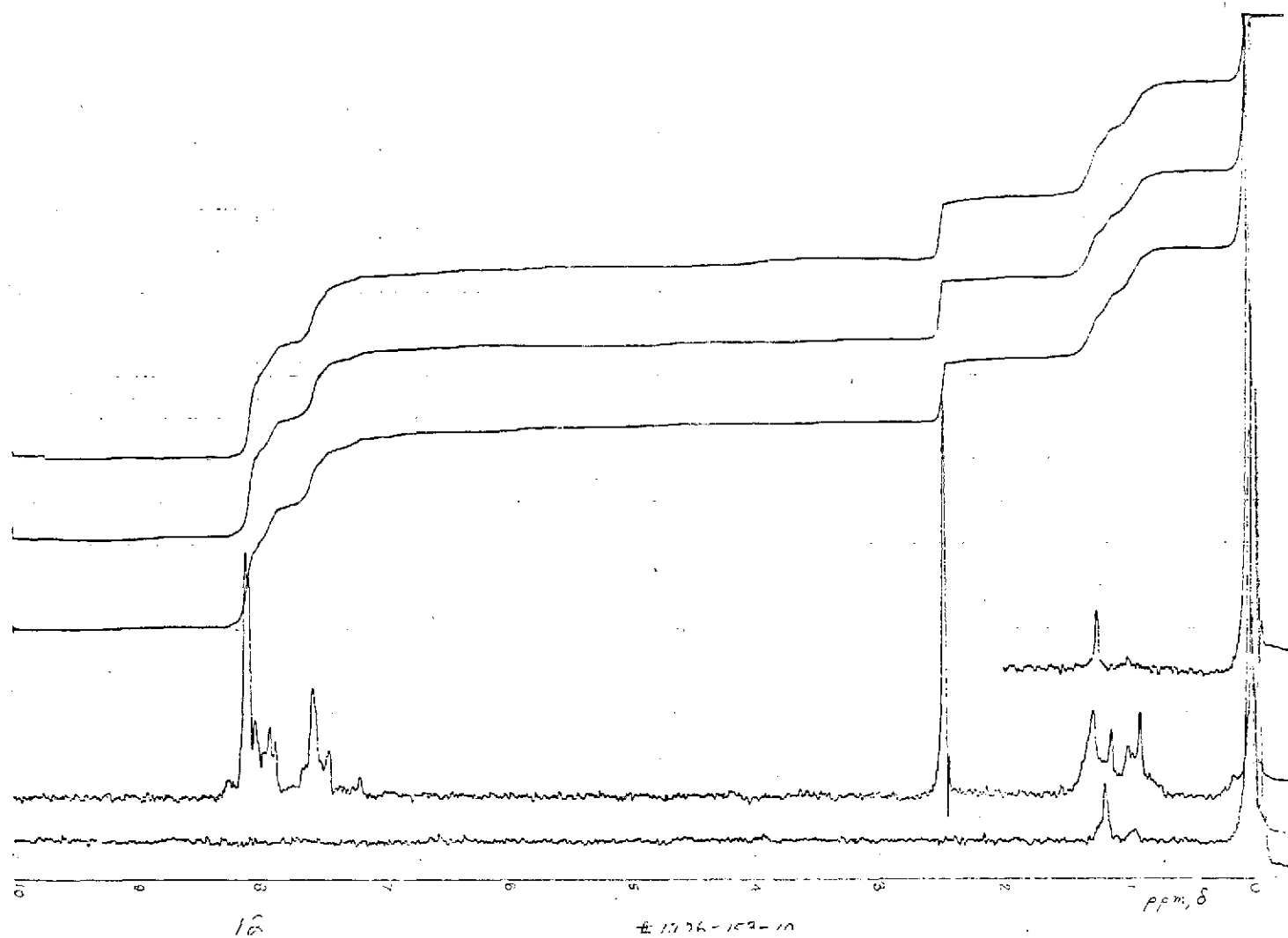


Figure 11. Nuclear Magnetic Resonance Spectrum of p-(Methyloxalyl)benzil (1206-153-10) in Carbon Tetrachloride.

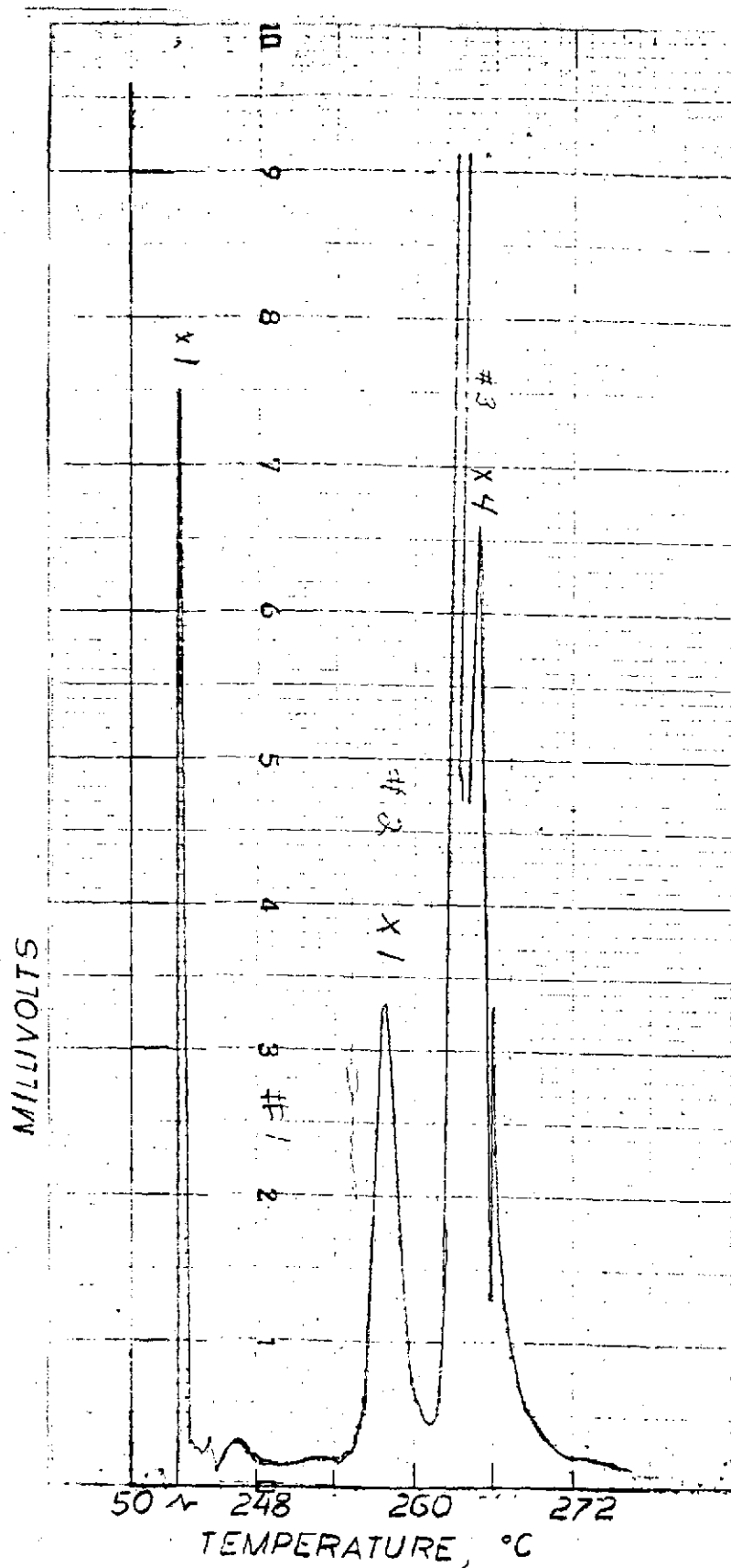


Figure 12. Gas Chromatogram of Compound 1206-153-10
(region between 56° and 248°C not shown).

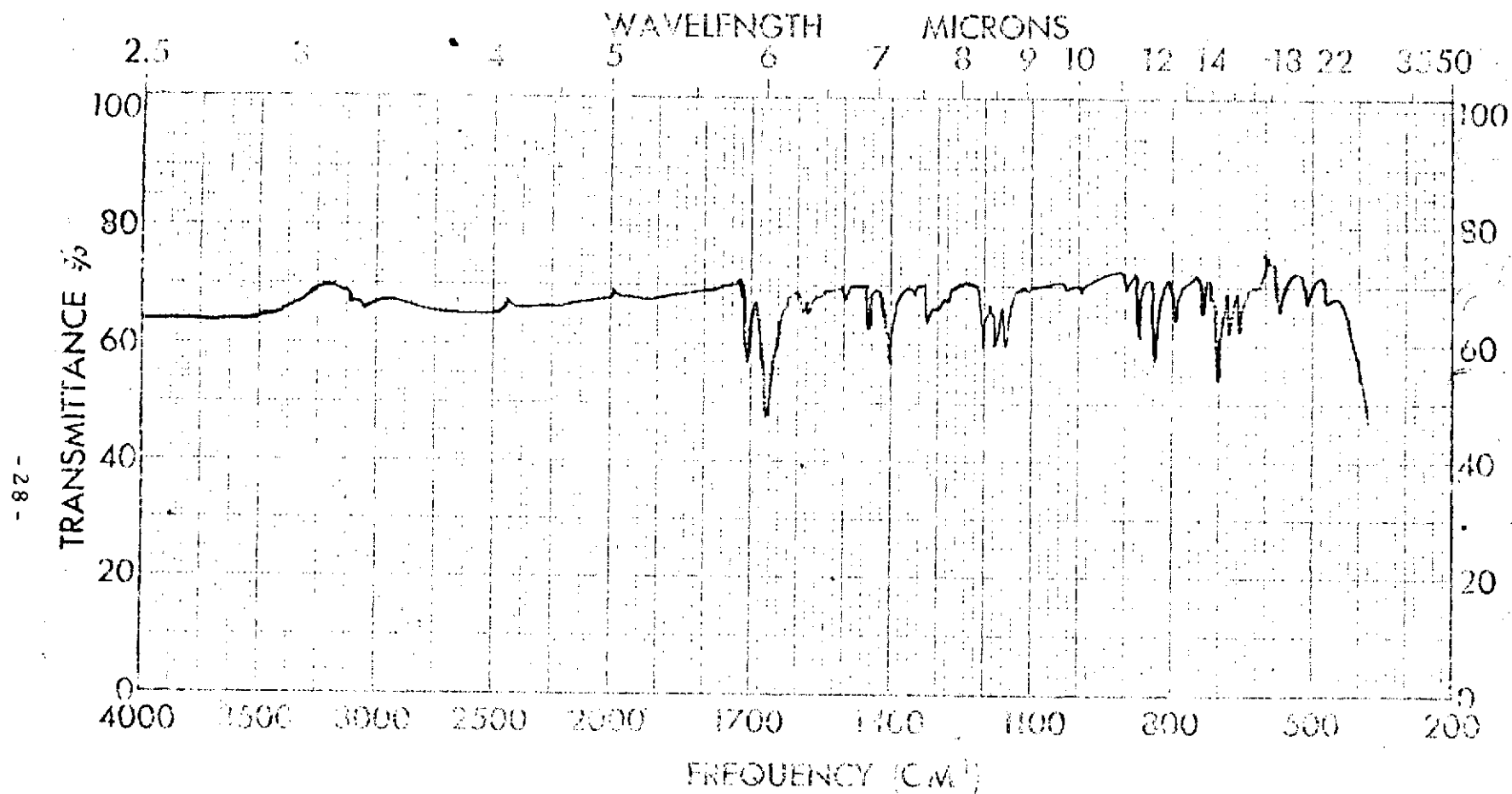
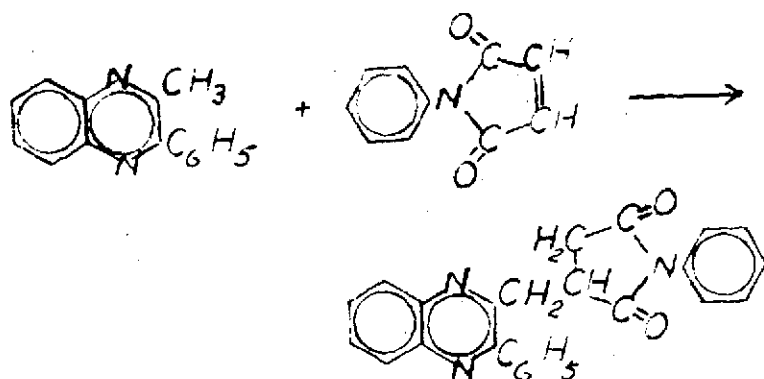


Figure 13. Infrared Spectrum of Compound 1206-153-10-GC1 p-(Methyloxalyl)benzil
Obtained by Gas Chromatography.



2-Methyl-3-phenylquinoxaline was prepared by refluxing for 5 hours a mixture of 4.61 g (0.0310 mole) 1-phenyl-1,2-propanedione, 3.44 g (0.0319 mole) o-phenylenediamine and 25 ml chloroform. The reaction solution was treated with 1 g decolorizing charcoal and filtered. The filtrate was cooled to -10°C . The crystals which formed were filtered off, washed with chloroform and dried giving 1.31 g of 1181-152-2 melting at $57-8^{\circ}\text{C}$. v. Auwers⁴⁵ reported the melting point of 2-methyl-3-phenylquinoxaline as $57-58^{\circ}\text{C}$. The filtrate from 1181-152-2 was concentrated to half volume and cooled. A second crop of 2-methyl-3-phenylquinoxaline (1181-152-4) weighing 2.2 g was obtained. The infrared spectrum of 2-methyl-3-phenylquinoxaline is shown in Figure 14.

A mixture of 0.4877 g (2.214×10^{-3} mole) 2-methyl-3-phenylquinoxaline and 0.3861 g (2.30×10^{-3} mole) N-phenylmaleimide was heated at 250°C for 2 hours. Since the reaction product melted at $92-100^{\circ}\text{C}$ which is above the melting point of either reactant, it is concluded that a reaction occurred. Hence, a Michael condensation as a cross-linking mode between polyquinoxalines bearing 2-methyl substituents and di-maleimides is considered probable.

Evidence from the literature provides additional support⁴⁶ for cross-linking via the Michael addition, A. A. Berlin et al are reported to have prepared polyquinoxalines from bis(2,3-dimethyl-6-quinoxaliny) and o-phenylene - and m-phenylenedimaleimide. "The reaction proceeded via formation of a donor-acceptor complex with a subsequent H migration to the imide molecule."

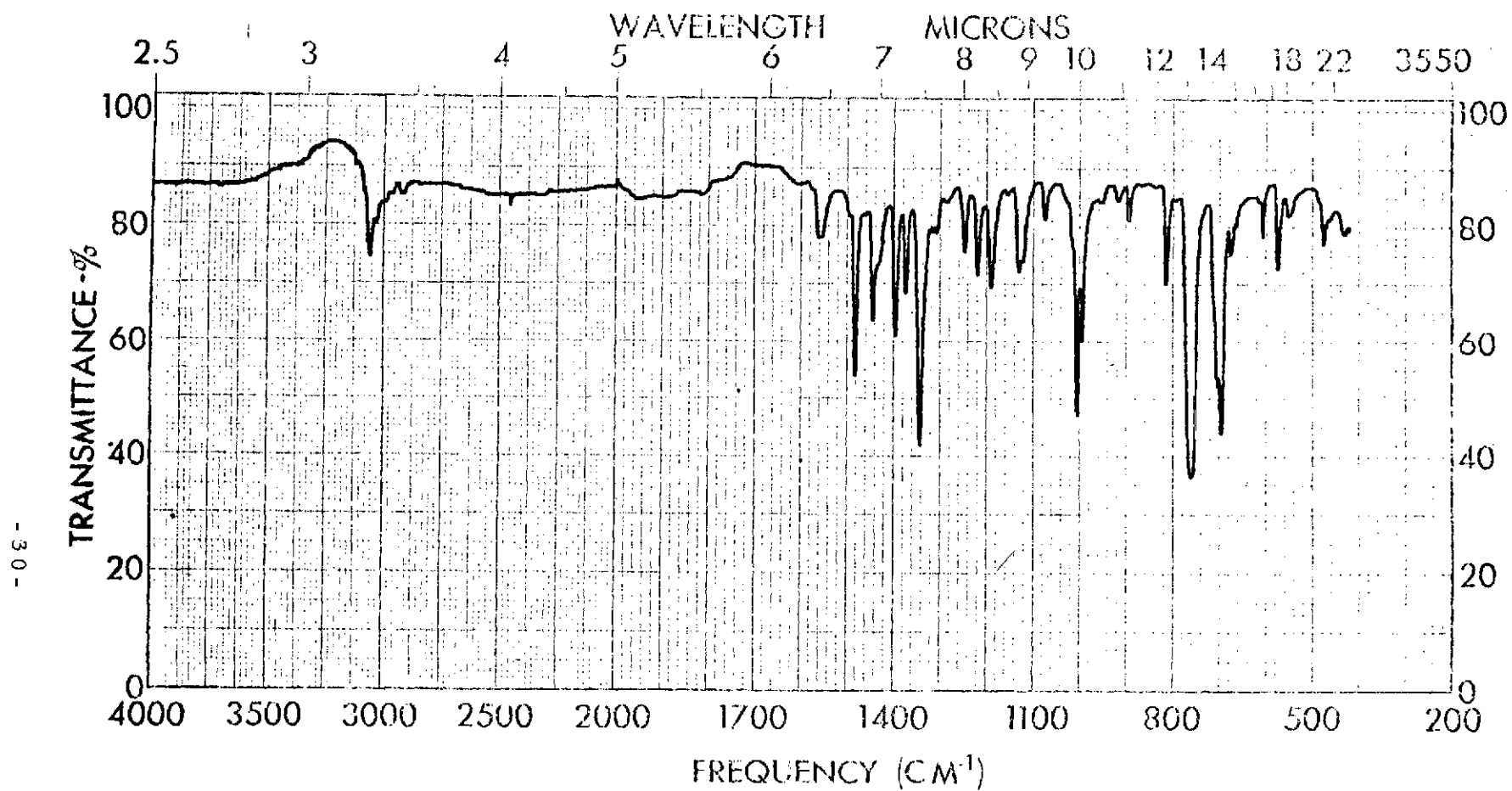


Figure 14. Infrared Spectrum of 2-Methyl-3-Phenylquinoxaline.

3. 3,3'-Diaminobenzidine

3,3'-Diaminobenzidine was recrystallized from methanol in a special apparatus comprising a hot-vapor Soxhlet extractor connected to a flask heated by an electric mantle and equipped with a nitrogen inlet and a 10 mm. bore stopcock acting as a drain. The stopcock was joined by a 50/50 standard taper inner glass joint to a cylindrical funnel equipped with a fritted disc and having a small stopcock at the bottom. The stopcock was connected through a rubber stopper to a suction flask.

A 20.7 g portion of commercial 3,3'-diaminobenzidine (m. p., 174 - 6°C, from Burdick & Jackson Laboratories, Inc.) and 0.3 g sodium hydrosulfite were placed into the extraction thimble and was extracted with 200 ml refluxing methanol for 8 hours while oxygen-free nitrogen was passed through the apparatus. After the mixture of crystals and methanol in the flask had cooled to room temperature, the large stopcock was opened. The mixture was drained into the cylindrical funnel and the crystals were collected on the fritted disc by suction filtration, washed with two 50 ml portions of methanol and dried under a flow of nitrogen. The purified 3,3'-diaminobenzidine melted at 176 - 7°C.

4. 3,3',4,4'-Tetraaminobenzophenone

75 g commercial 3,3',4,4'-tetraaminobenzophenone (m. p., 215 - 7°C from Burdick & Jackson Laboratories, Inc.) was dissolved in 300 ml refluxing dimethylformamide under a blanket of nitrogen and treated with 3 g Norit decolorizing charcoal. The mixture was filtered hot under nitrogen and the filtrate was cooled in ice and water. The crystals were filtered off, washed with 50 ml dimethylformamide and dried in vacuo while the temperature was slowly raised to 90°C. The yield was 62 g, m. p. 216.5 - 8.0°C.

5. 1,4-Phenylenedimaleimide

This compound was prepared by the method of Kovacic and Hein's⁴⁷ modification of Searle's⁴⁸ procedure.

a. 1,4-Phenylenedi(maleamic acid)

A solution of 58.8 g (0.6 mole) maleic anhydride in 150 ml warm chloroform was treated with a solution of 21.6 g (0.2 mole) p-phenylenediamine in warm dioxane added in small

portions while the mixture was stirred mechanically. A vigorous reaction occurred during each addition and a green-brown precipitate formed. The mixture was stirred and heated at a gentle reflux for 7 hours. The cooled mixture was filtered, washed with chloroform and was dried. The yield of the crude mixture of maleic anhydride and 1,4-phenylenedi(maleamic acid) was 77 g.

b. 1,4-Phenylenedimaleimide

A suspension of 74 g of the crude 1,4-phenylenedi(maleamic acid) and 15 g of fused sodium acetate in 150 ml acetic anhydride was slowly heated to the boiling point, and a gentle reflux was maintained for one hour. The solids slowly dissolved in the refluxing mixture and changed from yellow to dark brown. The resulting mixture was cooled, poured into 500 ml of ice and water and was filtered. The crude 1,4-phenylenedimaleimide, when dried, weighed 47.3 g (91.5%). It was purified by extracting 15 g with 150 ml refluxing o-dichlorobenzene in a Soxhlet extractor. When the o-dichlorobenzene solution cooled, crystals of 1,4-phenylenedimaleimide deposited and were filtered off and dried. The yield was 8.0 g, and the compound melted at $343 - 8^{\circ}\text{C}$. (Kovacic and Hein reported a melting point of $346 - 50^{\circ}\text{C}$.)

B. Preparation of Polymers and Copolymers

1. Poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)]quinoxaliny}^a

A flask containing a mixture of 1.0037 g (0.002268 mole) 1,4-bis[(1'-naphthalenyl)oxalyl]benzene and 0.4896 g (0.002285 mole) 3,3'-diaminobenzidine was flushed with dry nitrogen for 20 minutes. Ten ml m-cresol were then introduced and the mixture was stirred mechanically for one hour. The temperature was increased to 142°C , and the mixture was heated and stirred overnight. The solution was heated between 160 to 200°C for 1/2 hour; it was then vacuum distilled at a pot temperature of $175 - 185^{\circ}\text{C}$ while 7 ml of distillate were collected. The viscous residue was redissolved in 10 ml of m-cresol. The inherent viscosity of a 0.5% solution of the polymer in m-cresol was found to be 0.92 dl/g at 30°C . A test film for evaluation was prepared (Procedure 1) by casting the m-cresol solution onto a glass plate, allowing the m-cresol to evaporate by heating with a heat lamp and finally in an oven at 260°C for 4 hours.

^a The polymer segments are probably also oriented 7,7'-, 6,7'-, and 7,6'.

In a repeat preparation, 0.03000 mole of each monomer were mixed and dissolved in 100 ml freshly distilled m-cresol and heated in 1/2 hour to reflux under a nitrogen sweep. After being refluxed for 18 hours, the dark-red solution was cooled to room temperature. The inherent viscosity of a 0.5% solution of the polymer in m-cresol was 1.90 dl/g at 30°C. A 14 x 6 inch film was prepared (Procedure 2) by casting the polymer solution onto a level glass plate inside a mask, de-aerating the solution at low pressure, leveling the plate, and allowing the solvent to evaporate at room temperature until the film was essentially dry. It was removed from the plate, clamped between iron sheets and heated under a nitrogen sweep in an oven programmed to attain 371.1°C (700°F) in 18 hours, to maintain 371.1°C for 4 hours and to cool to room temperature in approximately 6 hours. The film was approximately 2 mils thick.

2. Poly{2,2'-(1,4-phenylene)-6,6'-bis(3-phenyl)quinoxaliny}^a

A flask containing 6.4285 g (0.03000 mole) 3,3'-diaminobenzidine and 10.2713 g (0.03000 mole) 1,4-bis(phenyloxalyl)benzene was flushed with nitrogen and 100 ml freshly distilled m-cresol was added. The mixture was stirred for one hour at room temperature during which time, a dark-red viscous solution warm to the touch formed. A film was cast by Procedure 2 (section B-1) but great difficulty was encountered in the de-aeration stage. Even when the reaction time was 1/2 hour, difficulty was encountered in removing all the air bubbles.

3. Poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)-co-(phenyl)-(50/50)]quinoxaliny}^a

This copolymer was prepared by two methods. In the first, a solution of 0.9982 g (0.002256 mole) 1,4-bis[(1'-naphthalenyl)oxalyl]benzene and 0.7716 g (0.002254 mole) 1,4-bis(phenyloxalyl)benzene were dissolved in 10 ml hot m-cresol, and the hot solution was added to a refluxing solution of 0.9674 g (0.004515 mole) 3,3'-diaminobenzidine in 4.4 ml m-cresol. The solution was refluxed for 1 hour and cooled to room temperature. A 14 x 6 in film of the copolymer was cast by Procedure 2. In the second method, 6.4281 g (0.03000 mole) 3,3'-diaminobenzidine, 6.6375 g (0.01500 mole) 1,4-bis[(1'-naphthalenyl)oxalyl]benzene and 5.1357 g

 a The polymer segments are probably also oriented 7,7'-, 6,7'-, and 7,6'.

(0.01500 mole) 1,4-bis(phenyloxalyl)benzene were dry mixed and dissolved in 100 ml m-cresol under nitrogen. The dark-red solution was refluxed and stirred for 18 hours, cooled to room temperature and a film cast onto a glass plate by Procedure 2.

4. Poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)-co-(phenyl)-(75/25)]quinoxaliny} ^a

A mixture of 6.4280 g (0.03000 mole) 3,3'-diaminobenzidine, 9.9563 g (0.02250 mole) 1,4-bis[(1'-naphthalenyl)oxalyl]benzene and 2.5676 g (0.00750 mole) 1,4-bis(phenyloxalyl)benzene was dry mixed under nitrogen and then dissolved in 100 ml m-cresol. The orange-red solution was heated to the boiling point and refluxed for 18 hours. After being cooled, the resulting solution was used to cast a film by Procedure 2.

5. Poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)-co-(phenyl)-(25/75)]quinoxaliny} ^a

A mixture of 6.4287 g (0.03000 mole) 3,3'-diaminobenzidine, 3.3183 g (0.00750 mole) 1,4-bis[(1'-naphthalenyl)oxalyl]benzene and 7.7031 g (0.02250 mole) 1,4-bis(phenyloxalyl)benzene was dry mixed under nitrogen and then dissolved in 100 ml m-cresol by heating to reflux. After 18 hours reflux, the solution was cooled to room temperature and was used to cast a film by Procedure 2.

6. Poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)-quinoxaliny-co-quinoxaliny]carbonyl(95/5)} ^a

A mixture of 0.3630 g (0.00150 mole) 3,3',4,4'-tetraaminobenzophenone, 6.1069 (0.02850 mole) 3,3'-diaminobenzidine and 13.2741 g (0.03000 mole) 1,4-bis[(1-naphthalenyl)oxalyl]benzene were dry-mixed under nitrogen and then dissolved in 100 ml m-cresol by heating to reflux. After 18 hours reflux, the solution was cooled to room temperature and was used to cast a film by Procedure 2.

- - - - -
^a The polymer segments are probably also oriented 7,7'-, 6,7'-, and 7,6'.

7. Poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)-quinoxaliny]carbonyl}^a

A mixture of 1.3883 g (3.1376×10^{-3} mole) 1,4-bis(1'-naphthalenyl)oxalylbenzene and 0.7615 g (3.1430×10^{-3} mole) 3,3',4,4'-tetraaminobenzophenone were charged into a 100 ml flask equipped with a condenser, an addition funnel, a mechanical stirrer and a nitrogen inlet tube. The system was flushed with pure nitrogen for 20 minutes prior to the start of the reaction. Thirteen ml m-cresol was then added and while a flow of nitrogen was maintained the bath temperature was raised to 145°C. The color of the mixture gradually changed from a yellow slurry to a dark-red, clear solution. The bath temperature was gradually increased to 210-13°C and the color changed to amber.

When the cooled solution was cast onto a glass plate, a brittle film formed which was unsuitable for test purposes.

8. Poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)-co-phenyl]-(50/50)quinoxaliny]carbonyl}^a

A mixture of 6.6379 g (0.01500 mole) 1,4-bis[(1'-naphthalenyl)-oxalyl]benzene, 5.1355 g (0.01500 mole) 1,4-bis(phenyloxalyl)benzene and 7.2686 g (0.03000 mole) 3,3',4,4'-tetraaminobenzophenone was dry-mixed under a stream of nitrogen, and 100 ml m-cresol was added. The mixture rapidly turned orange and then red. It was heated at a gentle reflux for 18 hours (bath temperature 170-226°C) under nitrogen. Because the inherent viscosity of the reaction product was low ($\eta_{inh} = 0.168$), 49.4 g of solvent was distilled from 103.7 g of the solution in an attempt to drive the reaction. However, the inherent viscosity did not increase. A film cast from the m-cresol solution was brittle and was unsuited for test purposes.

C. Characterization of Polymers and Copolymers

The polymers and copolymers were characterized with respect to the following parameters:

^a The polymer segments are probably also oriented 7,7'-, 6,7'-, and 7,6'.

1. Elemental analysis
2. Infrared spectrum
3. Inherent viscosity
4. Glass transition temperature
5. Thermogravimetric analysis
6. Isothermal weight loss
7. Solubility
8. Tensile properties
9. Time to rupture under sustained tensile loading

1. Elemental Analysis

An analysis for the carbon, hydrogen and nitrogen content was performed with an F & M model 185 Carbon, Hydrogen and Nitrogen Analyzer. When present, oxygen was calculated by difference. Table III lists the molar proportions of the monomers used, the theoretical C, H, N and O content and the found content for the polymers and copolymers prepared. In subsequent tables, reference is made to the material prepared by its specimen designation given in column 1 of Table III.

2. Infrared Spectrum

Figures 15 to 21 are the infrared spectra of the films of the polymers and copolymers synthesized. The specimen films were prepared by evaporating a 0.5% solution of the freshly prepared polymer in m-cresol onto the sodium chloride window. A heat lamp was used to aid the evaporation.

3. Inherent Viscosity

The inherent viscosities of the polymers prepared were determined at 30.0°C in a Cannon-Fenske Viscometer with a m-cresol solution obtained by diluting the polymer solution to approximately 0.5 g/100 ml. Actual concentrations were determined by evaporating an aliquot to dryness at 300°C and weighing the residue. Calculation of the inherent viscosity (η_{inh}) was made from the relationships:

TABLE III

ELEMENTAL ANALYSIS OF SOME QUINOXALINE POLYMERS AND COPOLYMERS

Specimen Designation	Monomer Composition, Mole %				Polymer Composition, Weight %							
					Theory				Found			
	N ^a	P ^b	D ^c	T ^d	C	H	N	O	C	H	N	O ^e
N100D100	100	0	100	0	86.28	4.14	9.58		85.73	4.90	8.89	0.48
N75P25D100	75	25	100	0	85.85	4.14	10.01		86.52	3.76	10.36	
N50P50D100 ^f	50	50	100	0	85.37	4.15	10.48		84.62	4.36	11.14	
N50P50D100 ^g	50	50	100	0	85.37	4.15	10.48		86.35	3.36	10.77	
N25P75D100	25	75	100	0	84.85	4.15	11.00		85.95	3.92	10.87	
P100D100	0	100	100	0	84.28	4.16	11.56		84.22	4.60	10.88	0.30
N100D95T5	100	0	95	5	86.26	4.14	9.58	0.02	85.85	4.36	10.36	

^a 1,4-Bis[(1'-naphthalenyl)oxalyl]benzene^b 1,4-Bis(phenyloxalyl)benzene^c 3,3'-Diaminobenzidine^d 3,3',4,4'-Tetraaminobenzophenone^e By difference^f Prepared by first procedure, Section III B 3^g Prepared by second procedure, Section III B 3

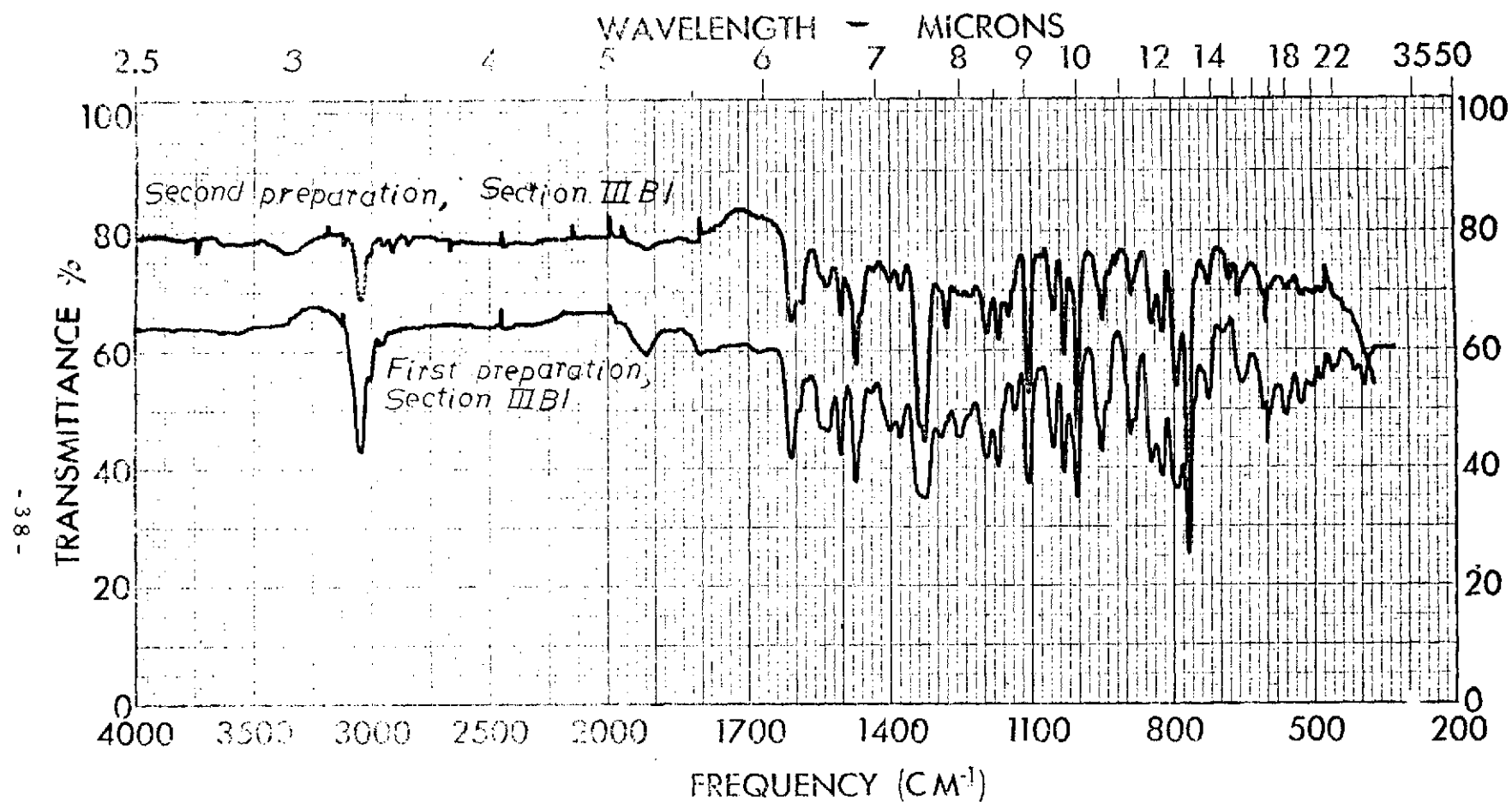


Figure 15. Infrared Spectrum of Polyquinoxaline N100D100.

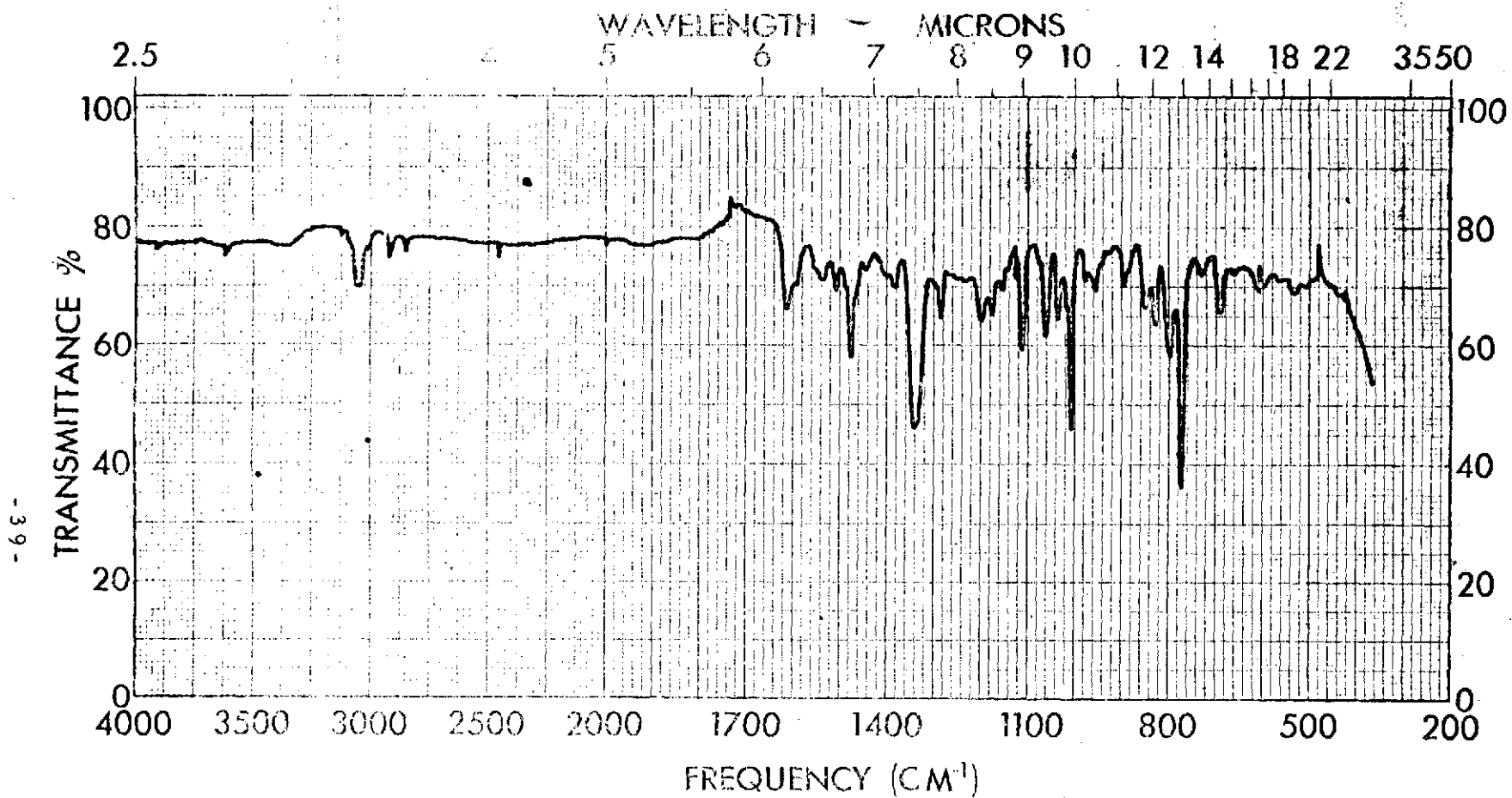


Figure 16. Infrared Spectrum of Polyquinoxaline N75P25D100.

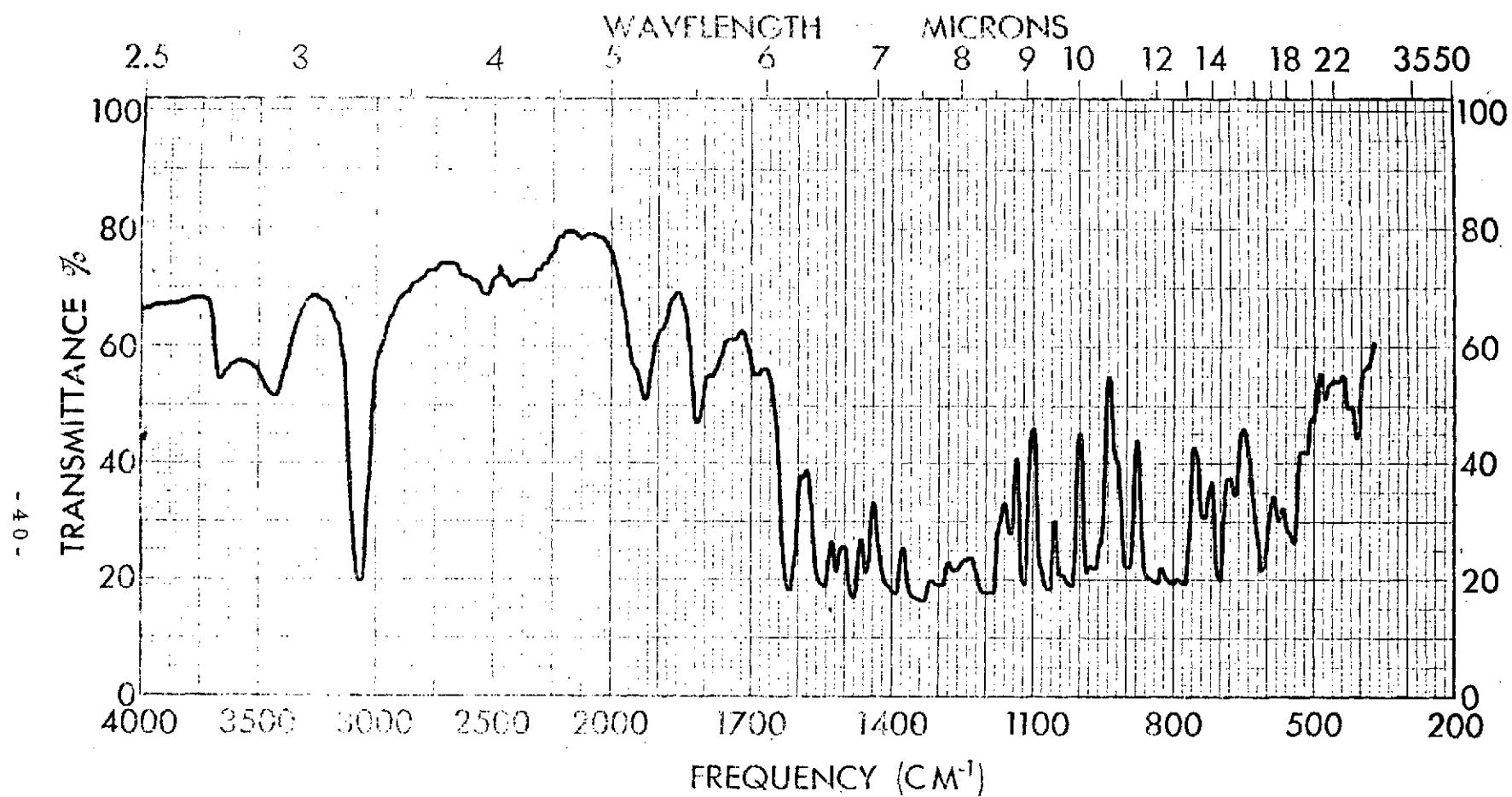


Figure 17. Infrared Spectrum of Polyquinoxaline N50P50D100 (First Preparation).

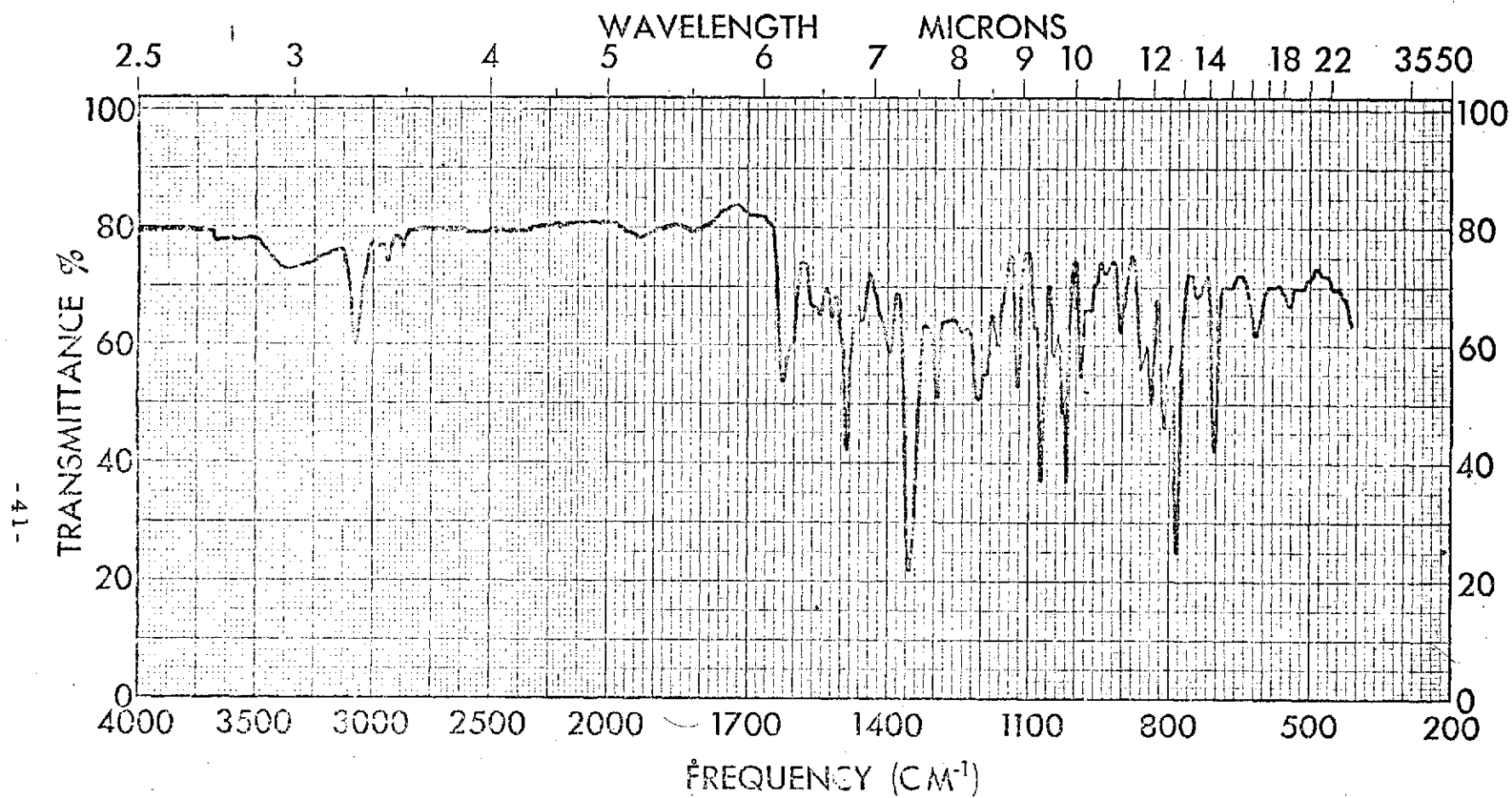


Figure 18. Infrared Spectrum of Polyquinoxaline N50P50D100 (Second Preparation).

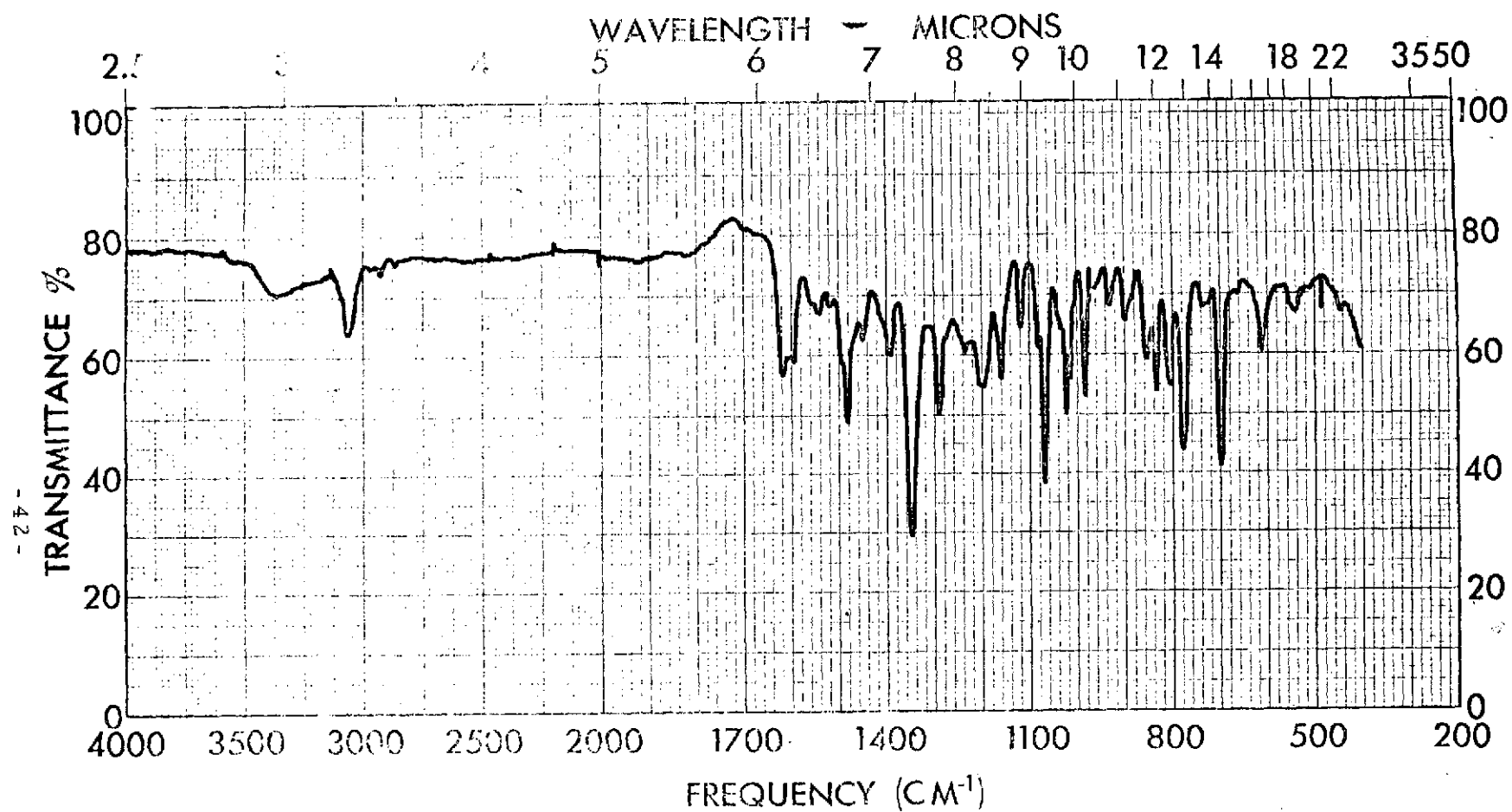


Figure 19. Infrared Spectrum of Polyquinoxaline N25P75D100.

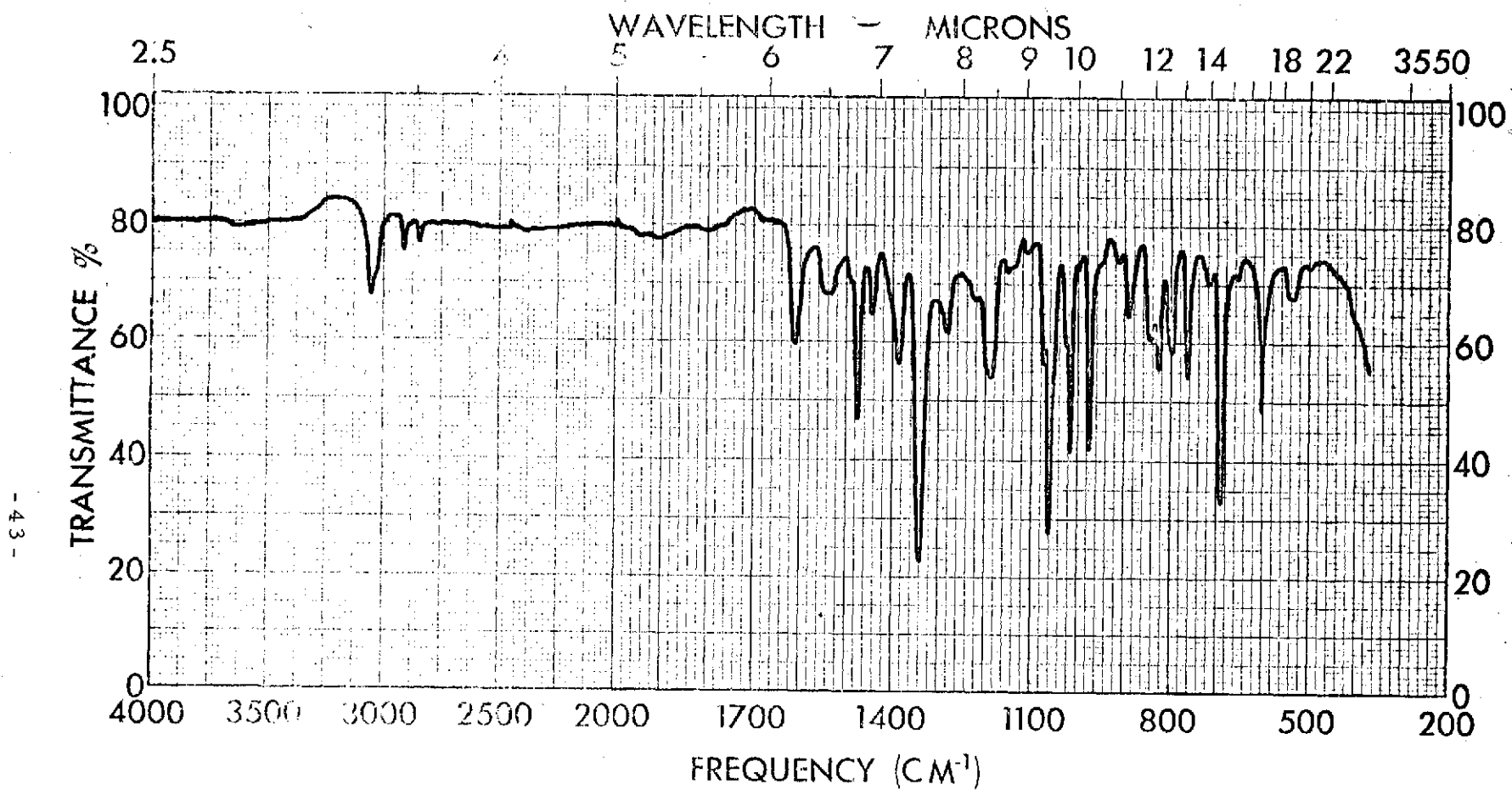


Figure 20. Infrared Spectrum of Polyquinoxaline Pl00D100.

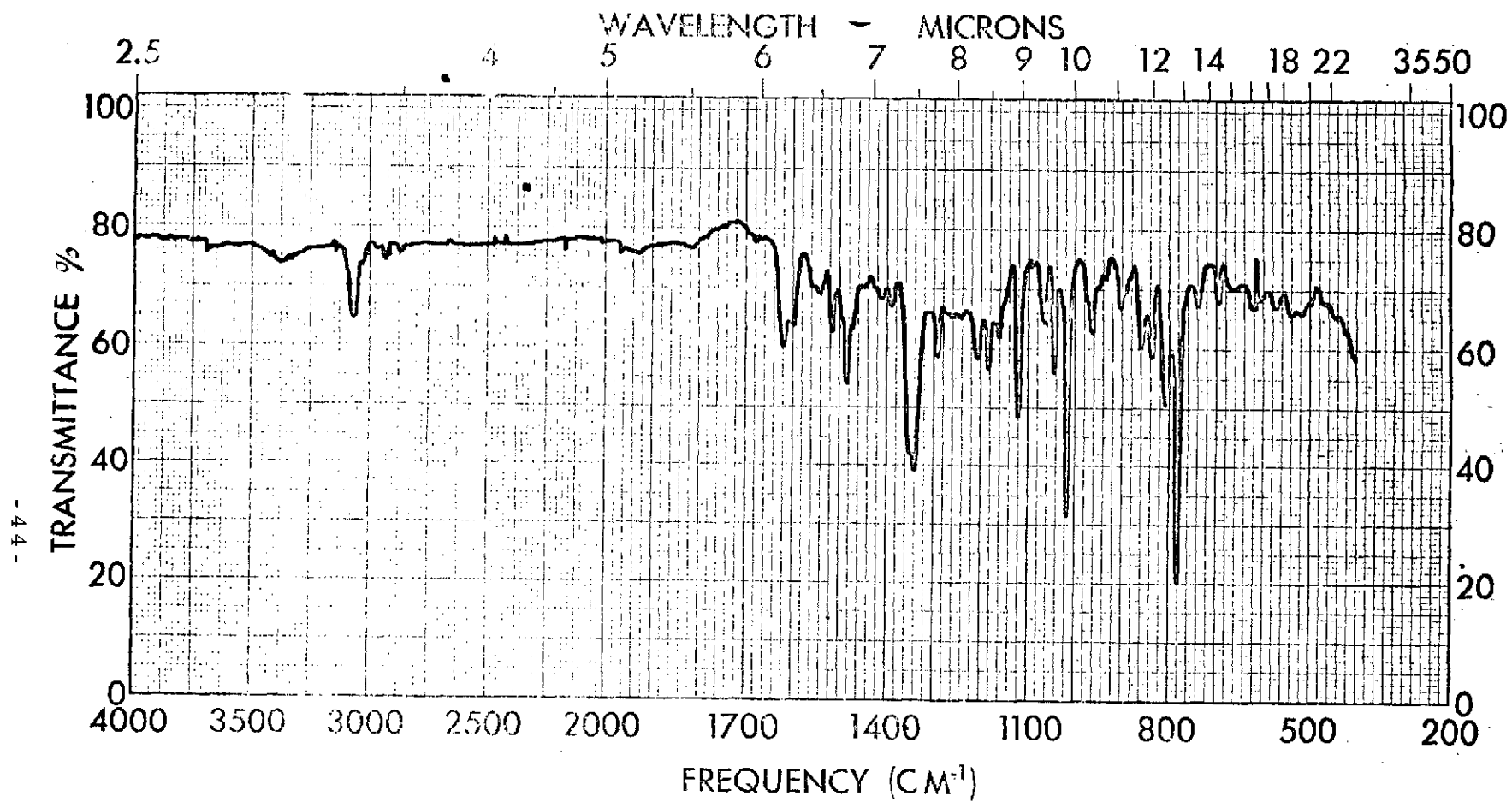


Figure 21. Infrared Spectrum of Polyquinoxaline N100D95T5.

$$\eta_{inh} = \frac{\ln \eta_{rel}}{C}$$

$$\eta_{rel} = t/t_o$$

where

η_{rel} = relative viscosity

t = efflux time of the polymer solution

t_o = efflux time of the solvent

C = polymer concentration in g/100 ml

Table IV lists the inherent viscosities of the several polymers and copolymers prepared.

4. Second-Order Phase Transition Temperature

Second-order phase transition temperatures were determined from stress-relaxation measurements by plotting the shift factor, $\log (1/K)$ as a function of the reciprocal of the absolute temperature and noting the temperature at which the slope of the shift function, $d[\log (1/K)]/d(1/T)$ changes. The method of determining the shift function is due to Schwarzl and Staverman⁴⁹ whose work is an extension of the WLF model⁵⁰. Transitions in the shift function have been attributed to second-order phase changes by Takayanagi⁵¹ and by Lander⁵².

The following procedure was used to determine the second-order transition temperatures; the procedure is exemplified with specimens taken from the polymer N100D100 prepared by the first method described in Section II B 1. Stress-relaxation curves were obtained at various temperatures in the range 23.9 - 426.7°C (75° to 800°F) by plotting the log of the stress required to maintain a given strain (e.g., a deflection of 20 mils in the case of specimen 1) at each temperature as a function of log time. In Figure 22, the stress-relaxation data at seven temperatures (for the sake of illustration) have been plotted. A "master curve" was then obtained by moving each curve along the log time axis until a smooth fit was obtained with the

TABLE IV

INHERENT VISCOSITIES OF SOME
QUINOXALINE POLYMERS AND COPOLYMERS

Specimen Designation ^a	η_{inh} dl/g at 30.0°C
N100D100 ^b	0.92
N100D100 ^b	1.90
N75P25D100	2.30
N50P50D100 ^c	0.96
N50P50D100 ^d	2.41
N25P75D100	2.44
P100D100	2.95
N100D95T5	1.15

^a See Table III for code of identification

^b See Section III B 1

^c Prepared by first procedure, Section III B 3

^d Prepared by second procedure, Section III B 3

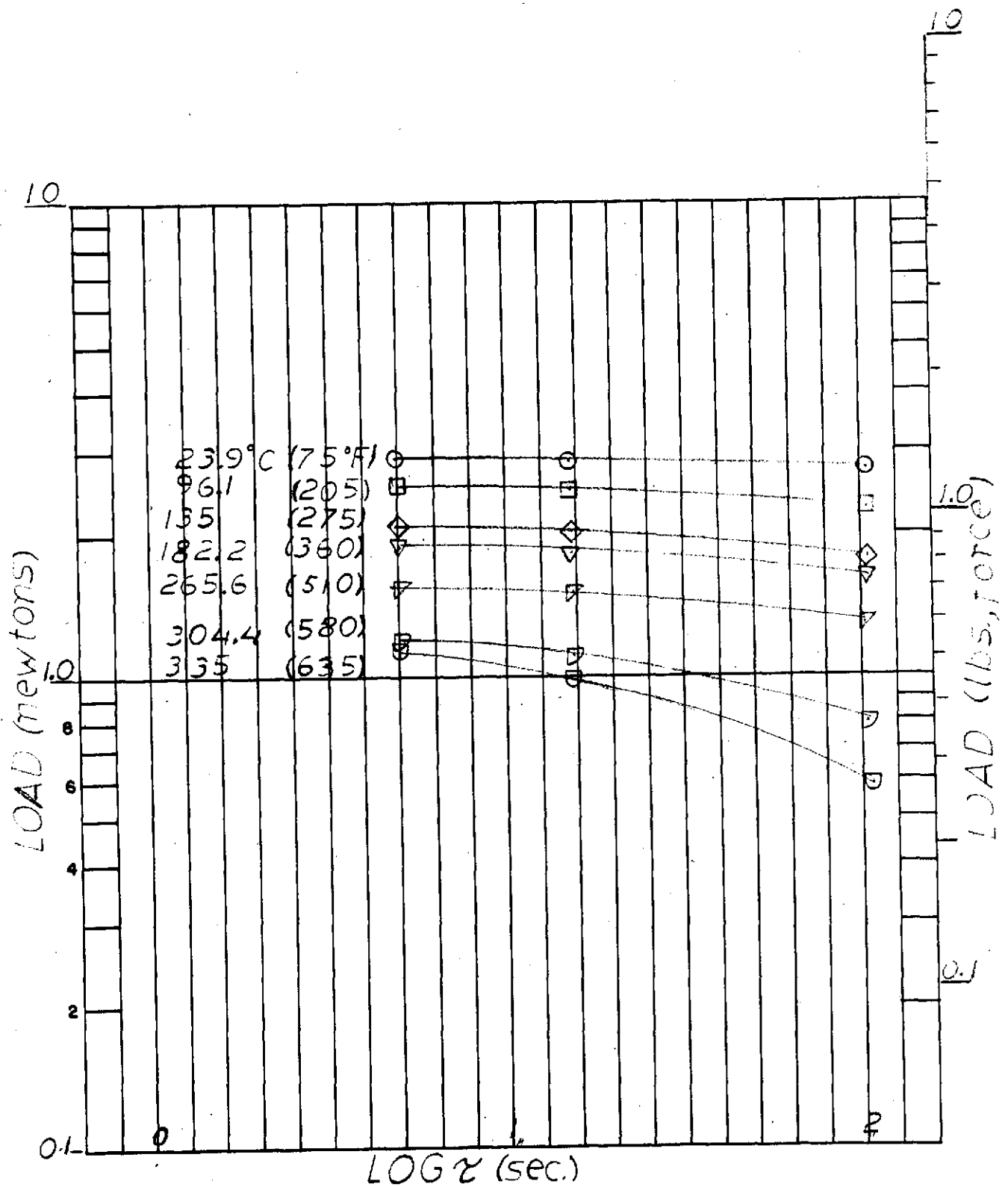


Figure 22. Stress-Relaxation Studies of N100D100.



23.9°C (75°F) curve (the reference temperature). The number of units (the shift factor) on the log time scale required for the shift for each temperature was noted. Figures 23 and 24 are master curves for specimen 1 and 2 respectively, and the shift in the log time scale is noted at each temperature as $\log (1/K)$.

The next step is to establish how the shift factor varies with temperature. For materials which do not undergo a phase change in the temperature range of interest, there is considerable justification to expect that the shift factor will follow an Arrhenius type of activation. In other words, the shift function will be of the form:

$$(1/K) = Ae^{-B/T}.$$

Therefore, a plot of $\log (1/K)$ versus the reciprocal of absolute temperature should be linear, with a slope of B and an intercept of A. If a phase change occurs within the temperature range of interest, one would expect a plot of $\log (1/K)$ versus the reciprocal of absolute temperature would depart from linearity and exhibit a different slope or activation energy for the different phases.

In Figure 25 the shift factor is plotted as a function of the reciprocal of the absolute temperature for samples of 1 and 2. Changes in the shift function occur at about 232.2°C (450°F) and 304.4°C (580°F) for specimen 1 and at about 254.4°C (490°F) and 310°C (590°F) for specimen 2.

Table V lists the second-order transition temperatures for some of the polymers and copolymers prepared. It will be noted that two second-order transitions were found for most of the materials.

5. Thermogravimetric Analysis

Figures 26 through 37 are thermograms obtained in the thermogravimetric analysis performed in helium and in air at a heating rate of 5°C/minute of the quinoxaline polymers prepared. In general, decomposition and oxidation remain below 2% at temperatures below 500°C. Decomposition (in helium) becomes significant above 600°C and oxidation is pronounced. Generally, the copolymers are less resistant to decomposition and to oxidation than are the homopolymers at and above 600°C. At 700°C, although increasing the phenylquinoxaline content of the copolymer increases the oxidation resistance, all the polymers are more than 50% oxidized.

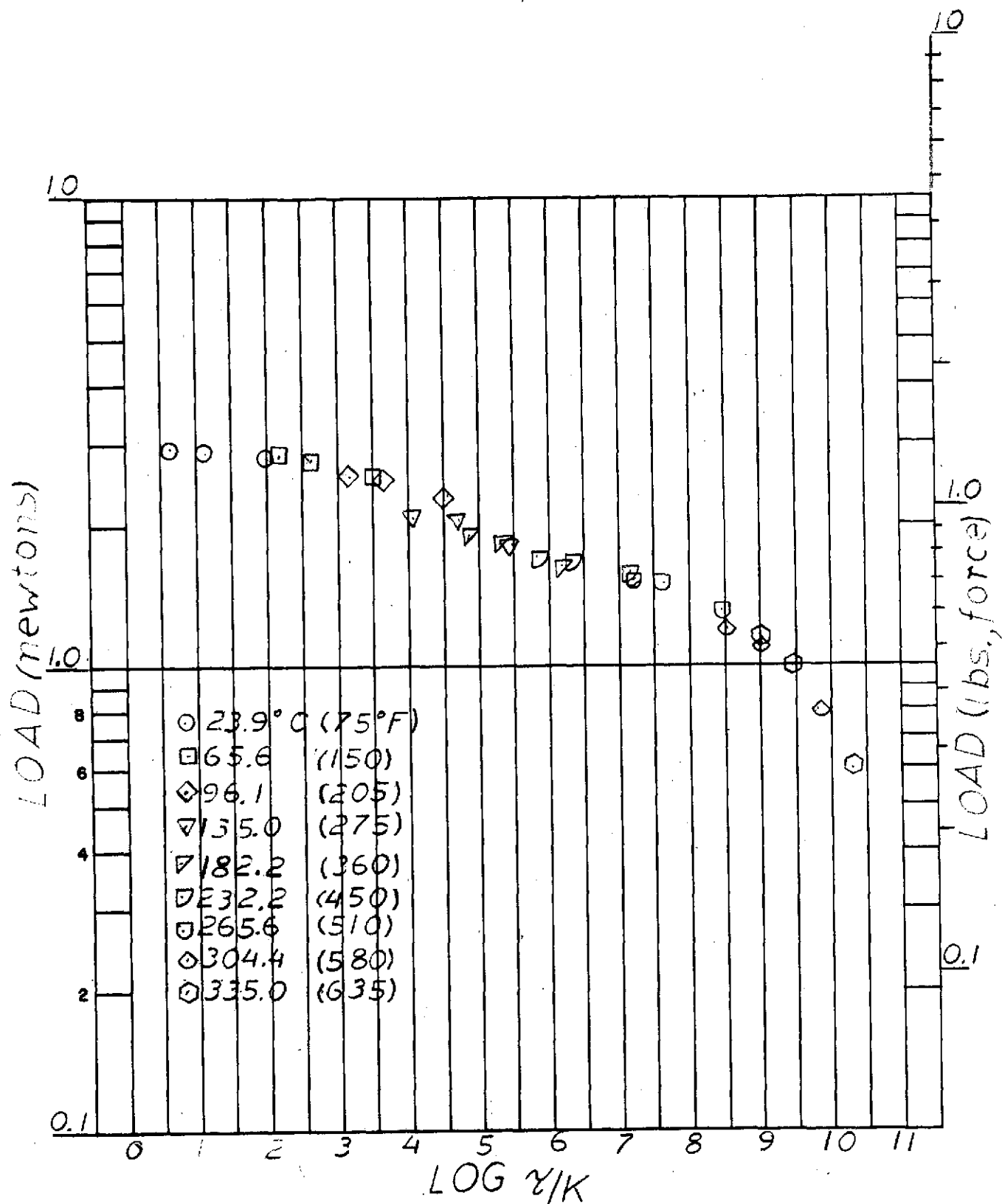


Figure 23. Master Curve for Specimen 1 of N100D100.

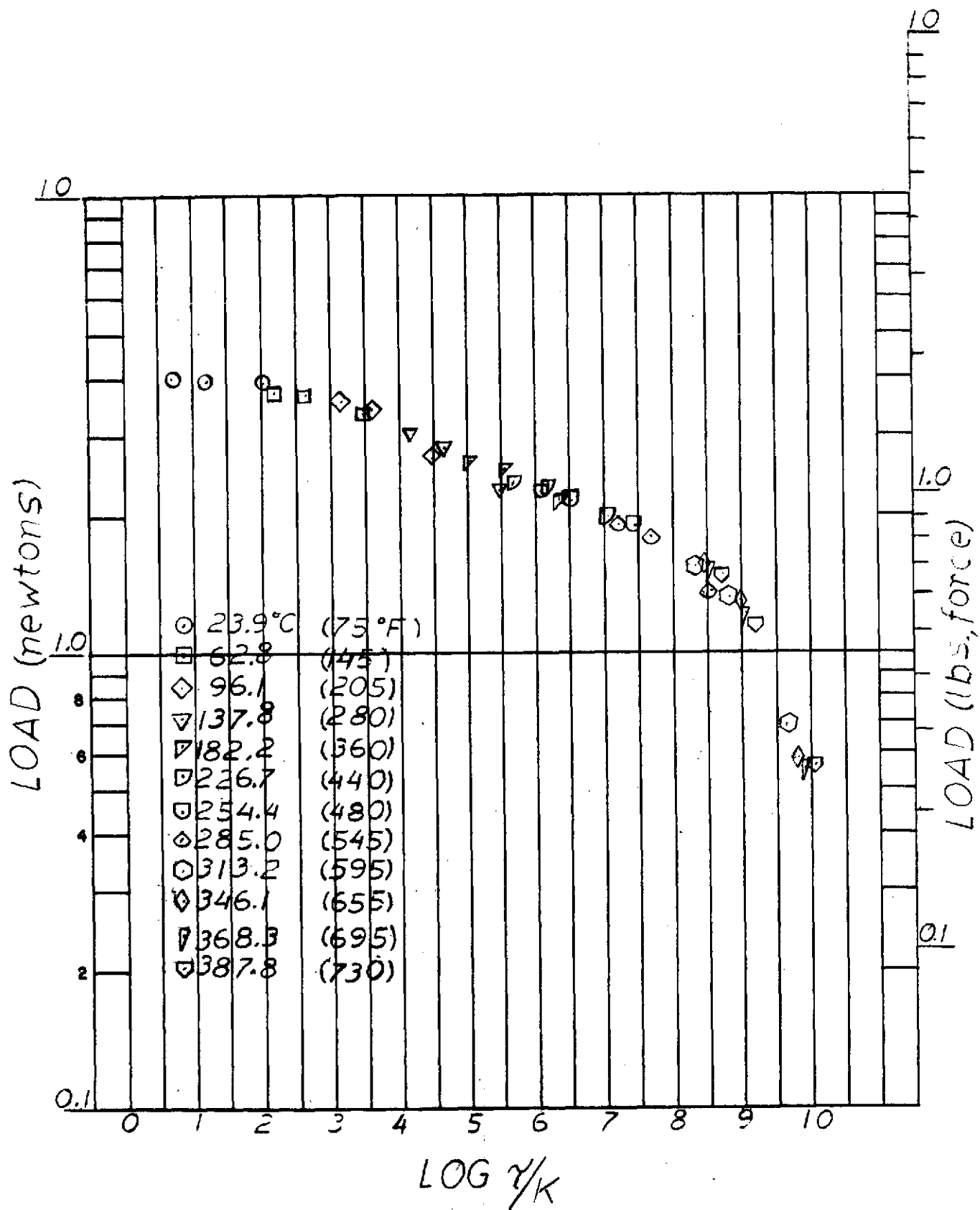


Figure 24. Master Curve for Specimen 2 of N100D100.



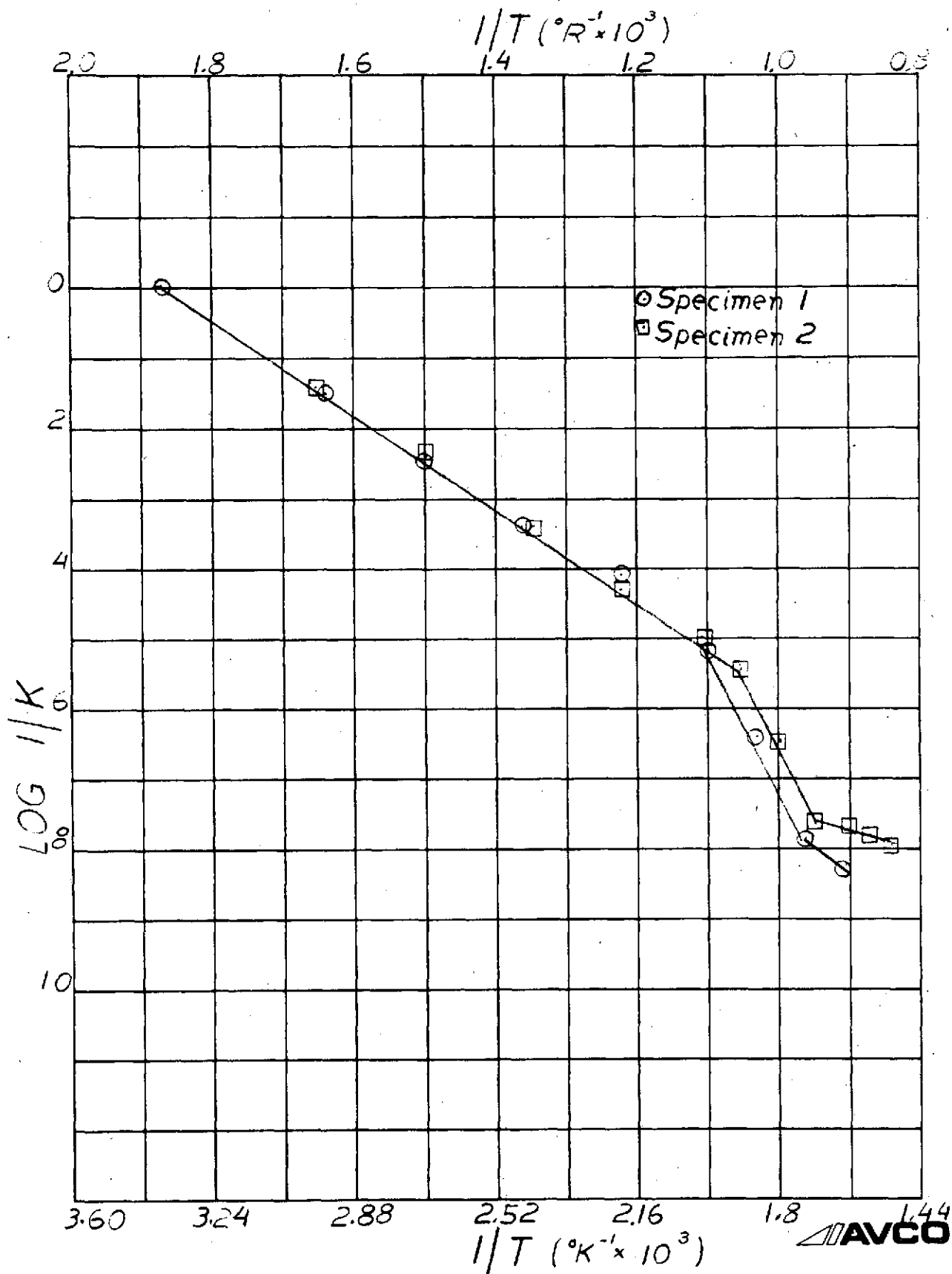


Figure 25. Determination of Second-Order Transition Temperature from Log $1/K$ vs. $1/T$ Plots for Specimens of NI00D100.

TABLE V
SECOND-ORDER PHASE TRANSITION TEMPERATURES OF
SOME QUINOXALINE POLYMERS

Specimen Designation ^a	Second-Order Phase Transition Temperatures °C (°F)	
	1	2
N100D100 ^b	232.2 (450) ^e	304.4 (580) ^e
	254.4 (490) ^e	310.0 (590) ^e
N100D100 ^c	215.6 (420)	326.7 (620)
N75P25D100	204.4 (400)	343.3 (650)
N50P50D100 ^d	182.2 (360)	310.0 (590)
N25P75D100	---	265.6 (510)
P100D100	226.7 (440)	337.8 (640)
N100D95T5	---	323.9 (615)

- ^a See Table III for code of identification
- ^b Prepared by first procedure, Section III B 1
- ^c Prepared by second procedure, Section III B 1
- ^d Prepared by second procedure, Section III B 3
- ^e Results of two tests

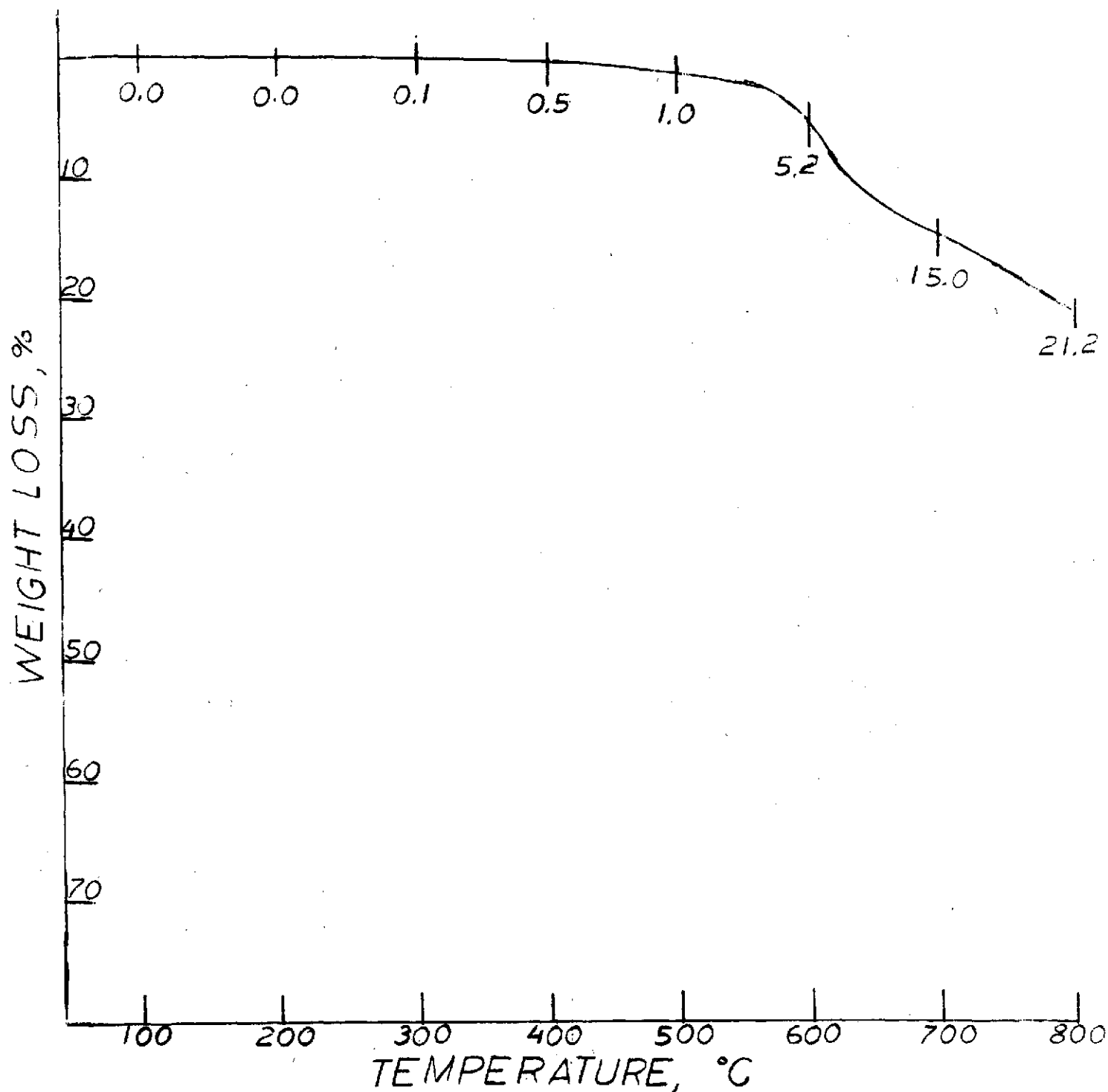


Figure 26. Thermogram of N100D100 in Helium.

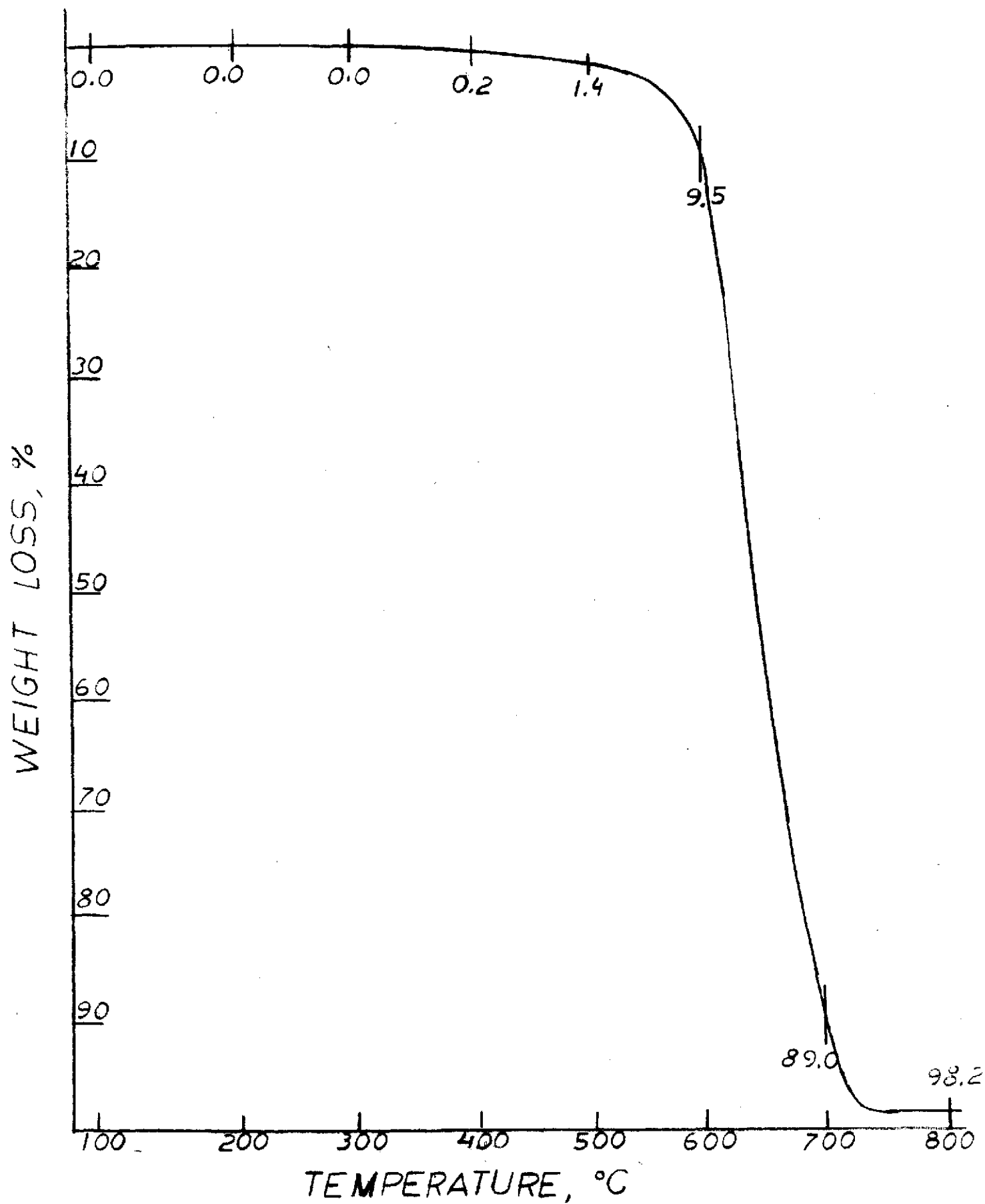


Figure 27. Thermogram of N100D100 in Air.

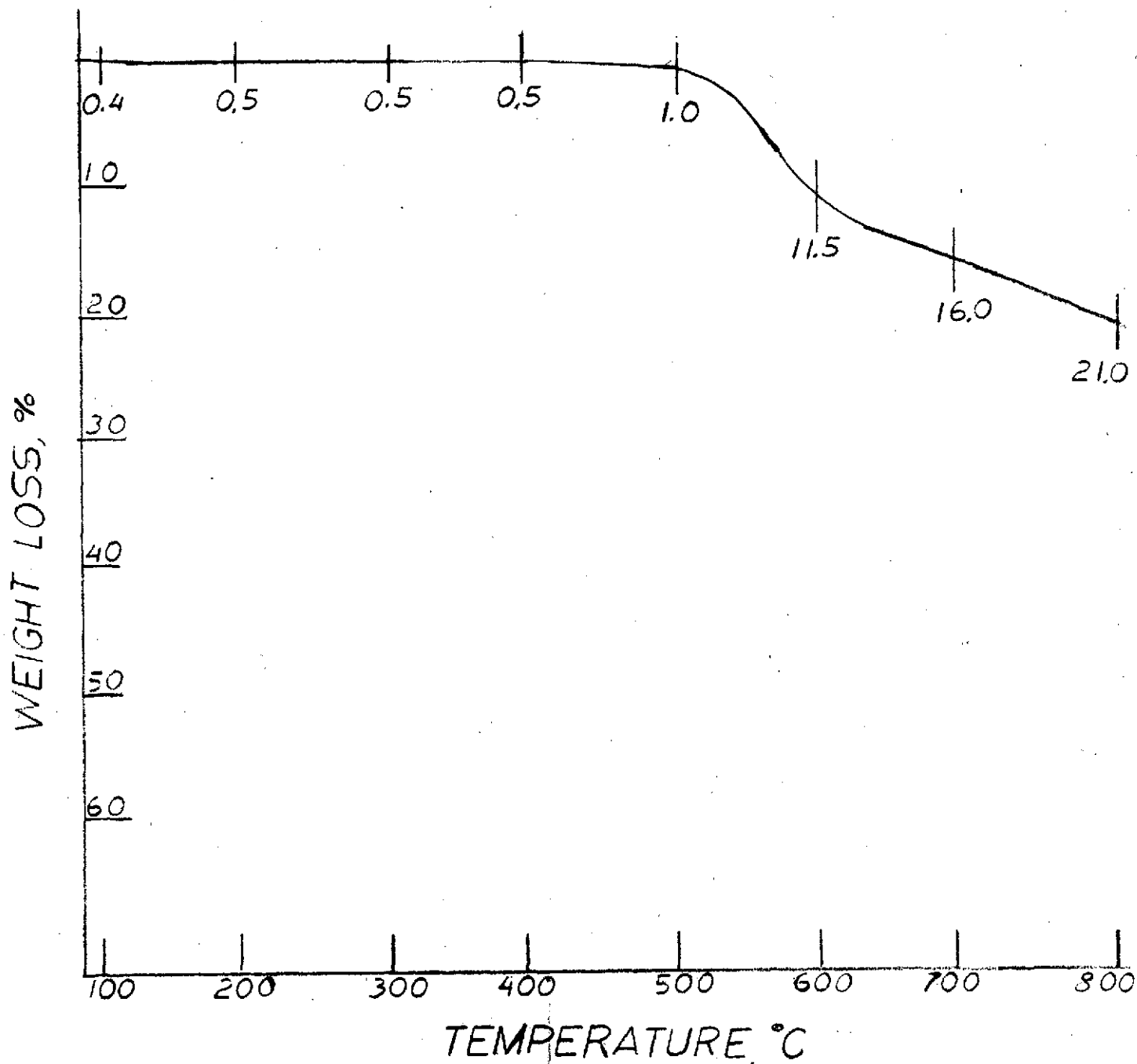


Figure 28. Thermogram of N75P25D100 in Helium.

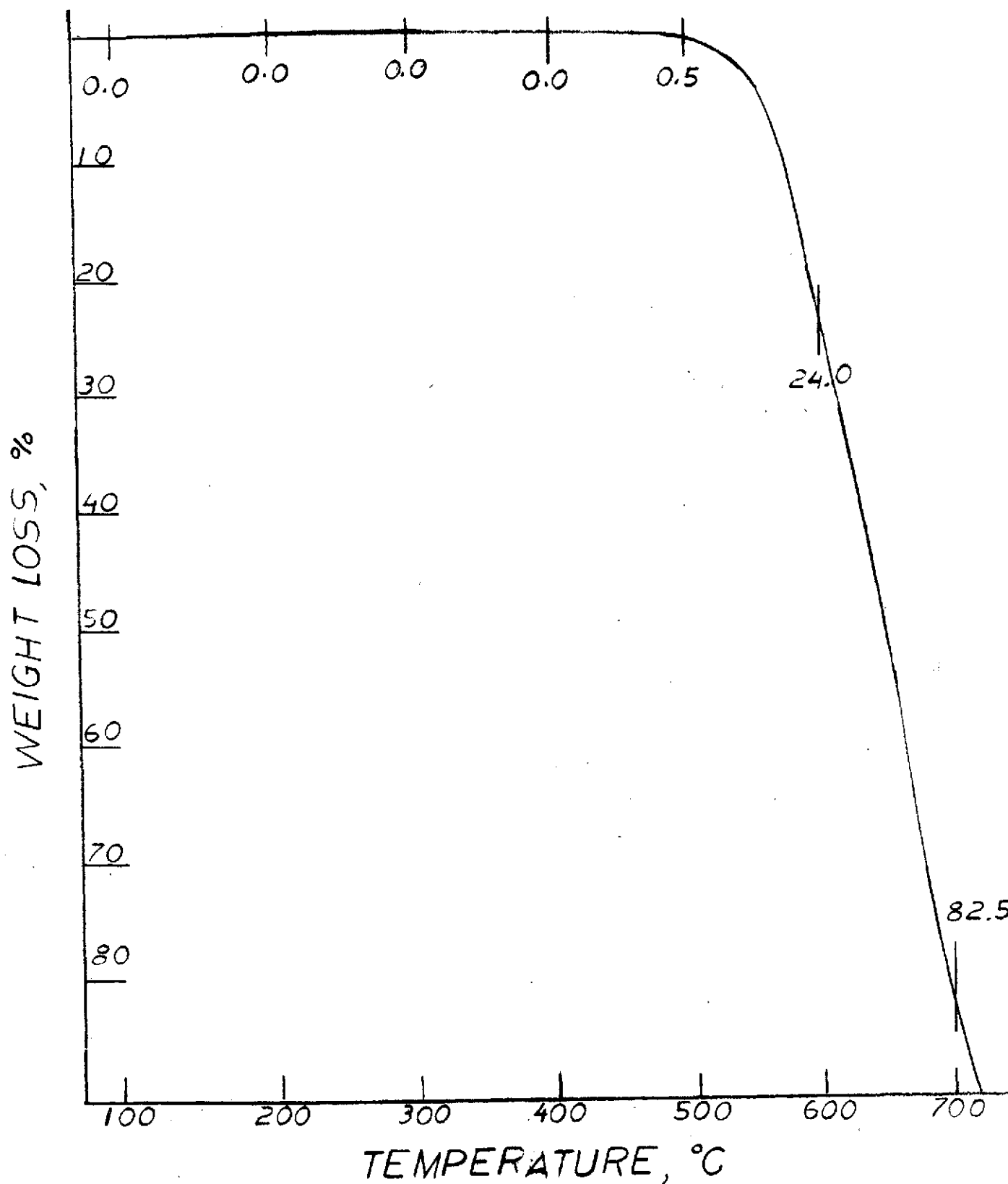


Figure 29. Thermogram of N75P25D100 in Air.

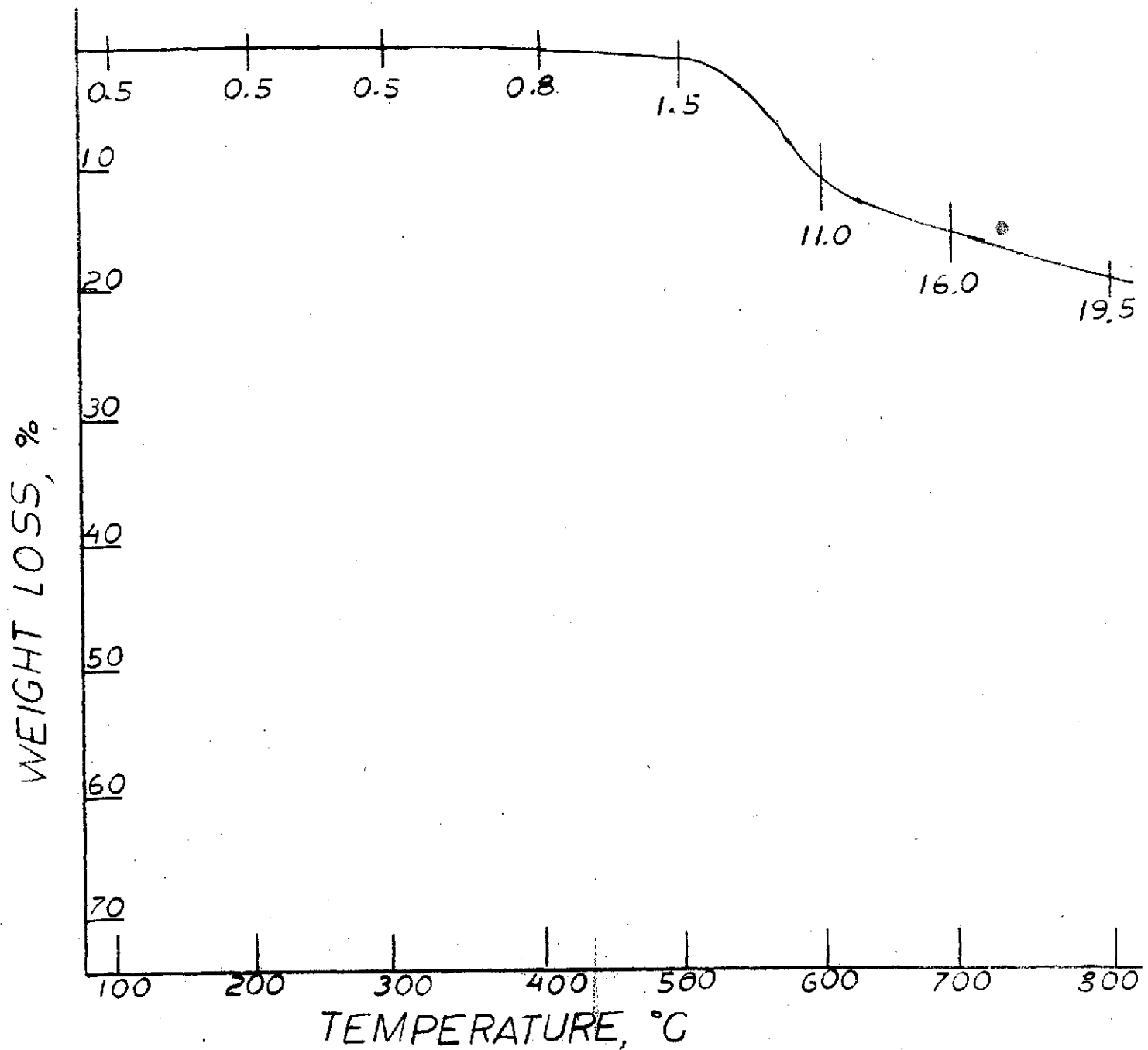


Figure 30. Thermogram of N50P50D100 in Helium.

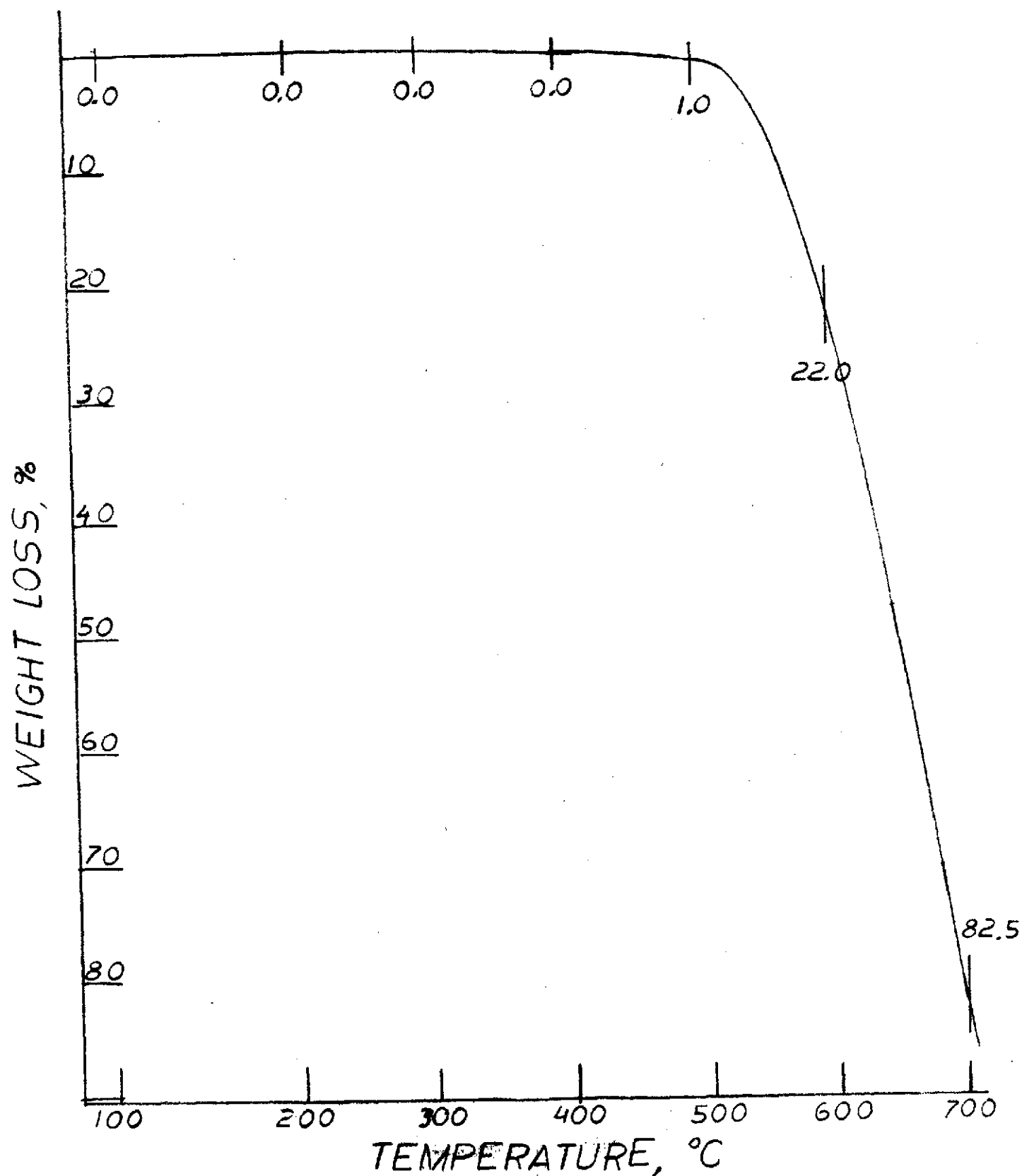


Figure 31. Thermogram of N50P50D100 in Air.

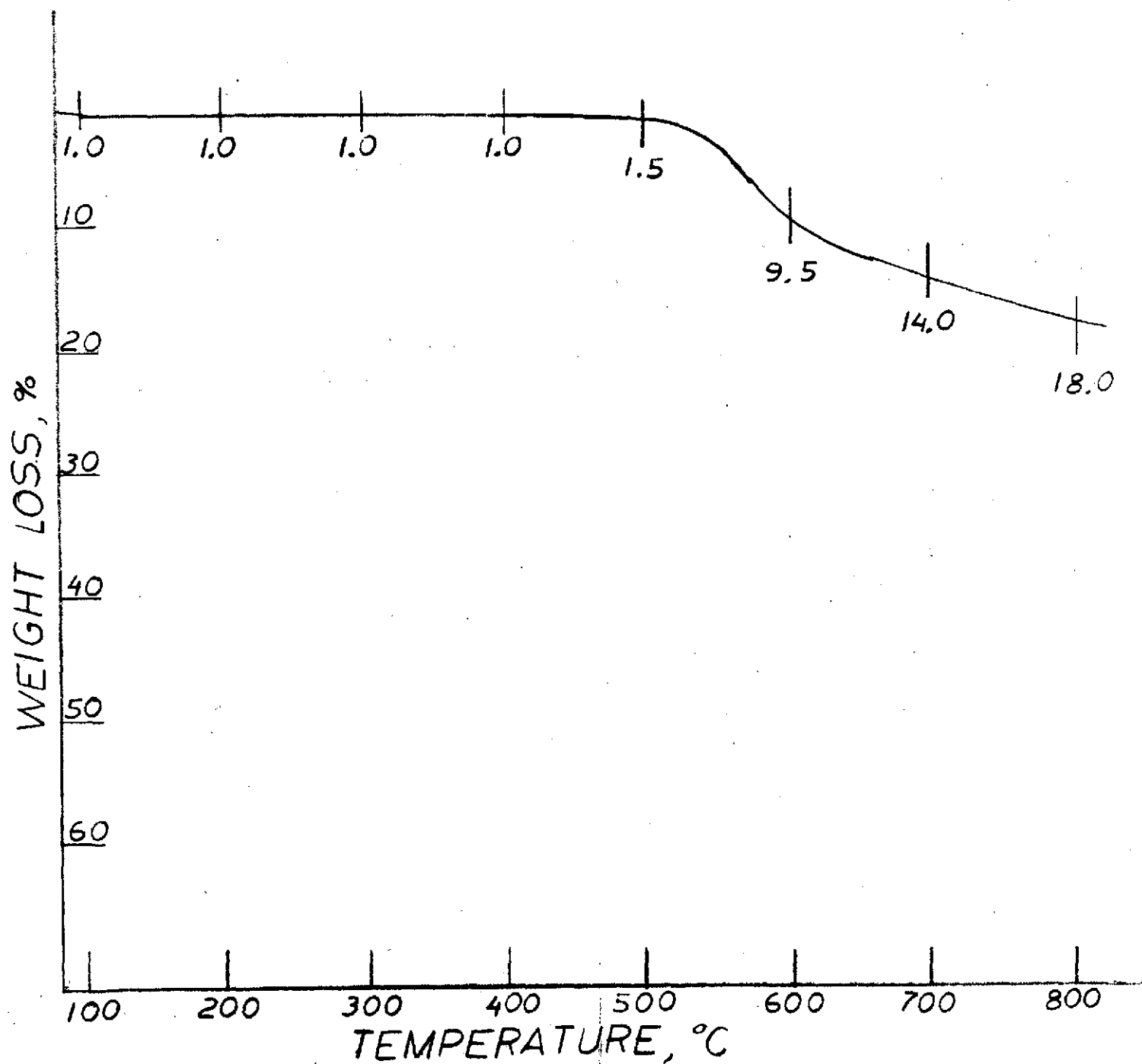


Figure 32. Thermogram of N25P75D100 in Helium.

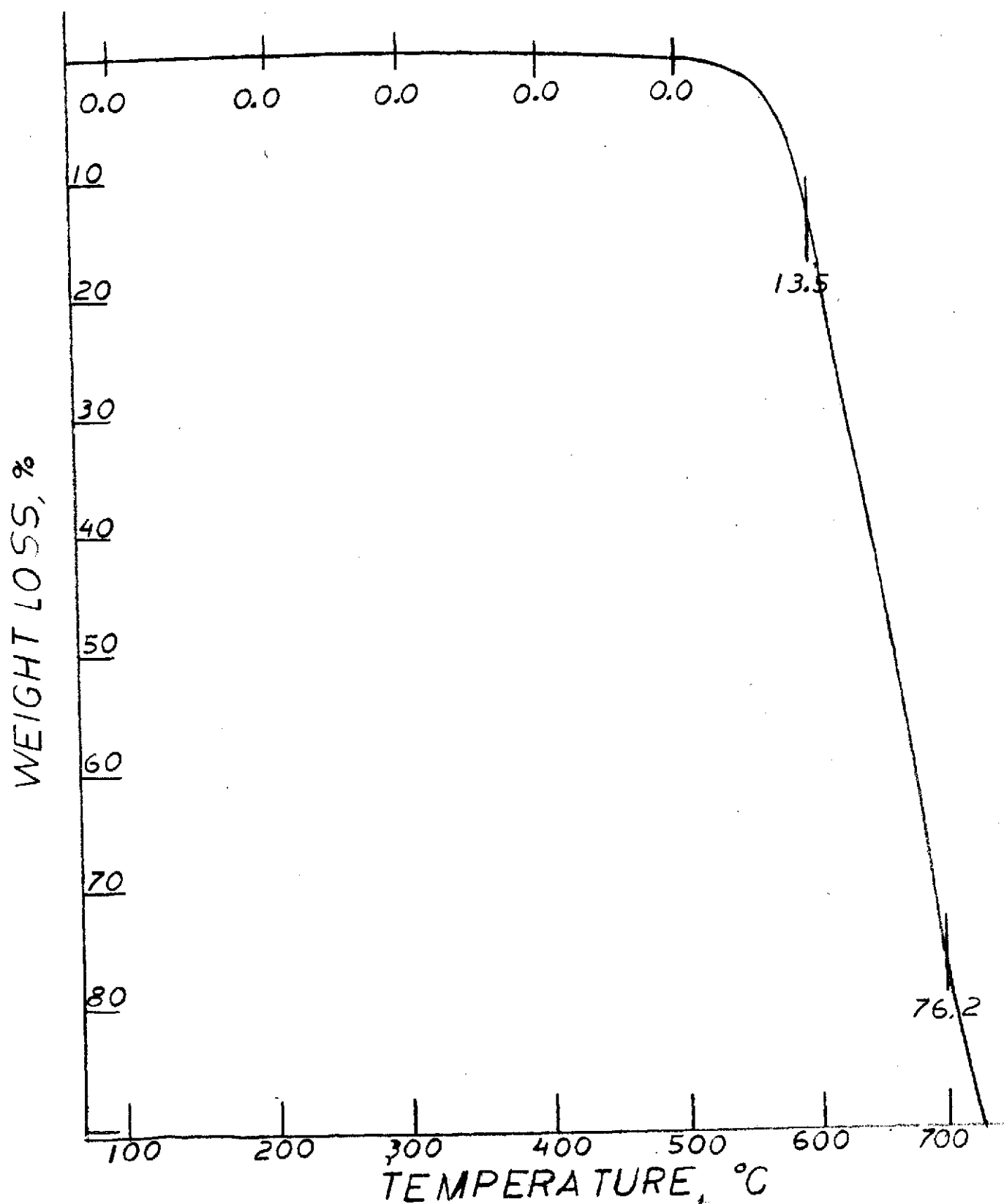


Figure 33. Thermogram of N25P75D100 in Air.

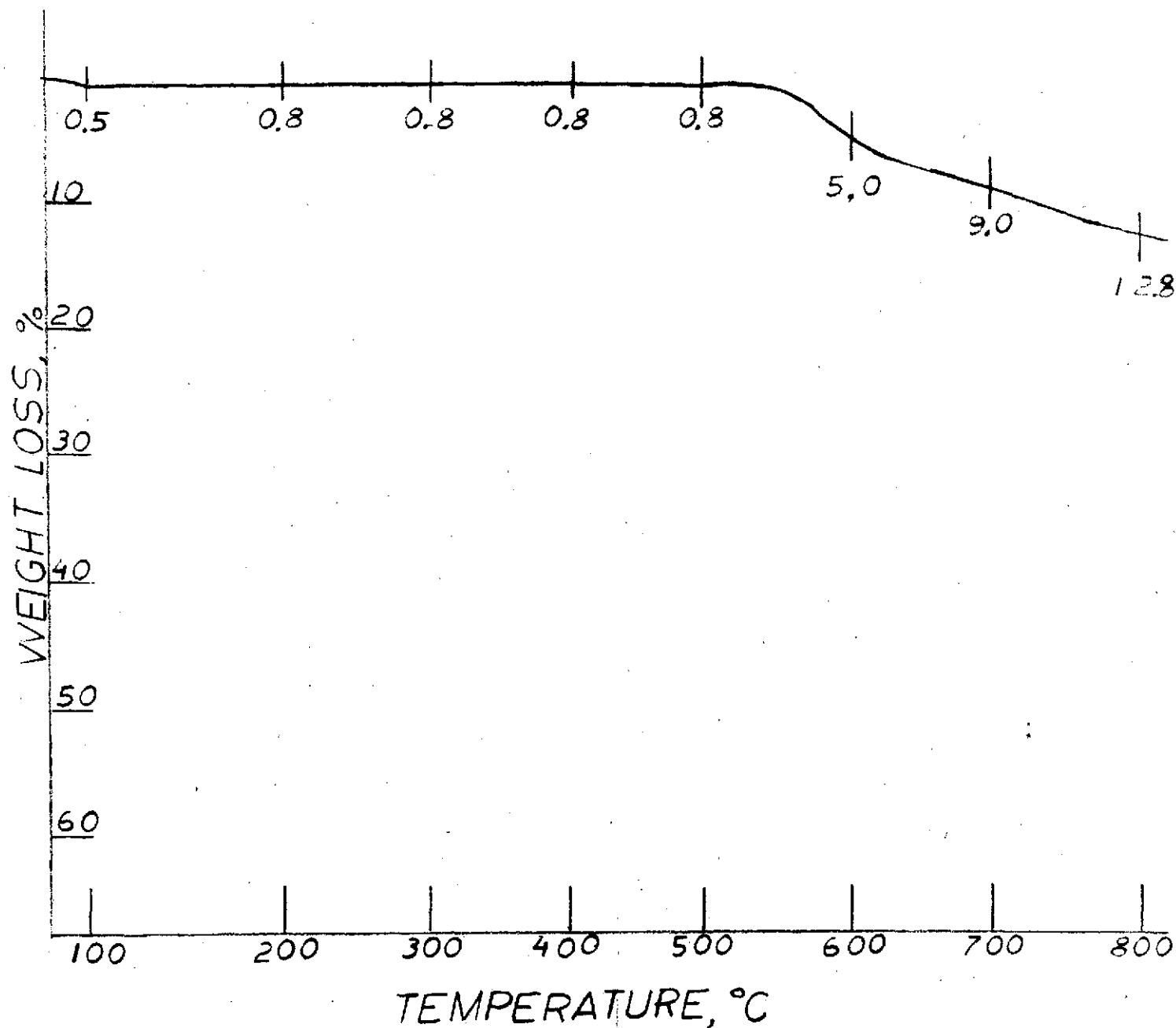


Figure 34. Thermogram of P100D100 in Helium.

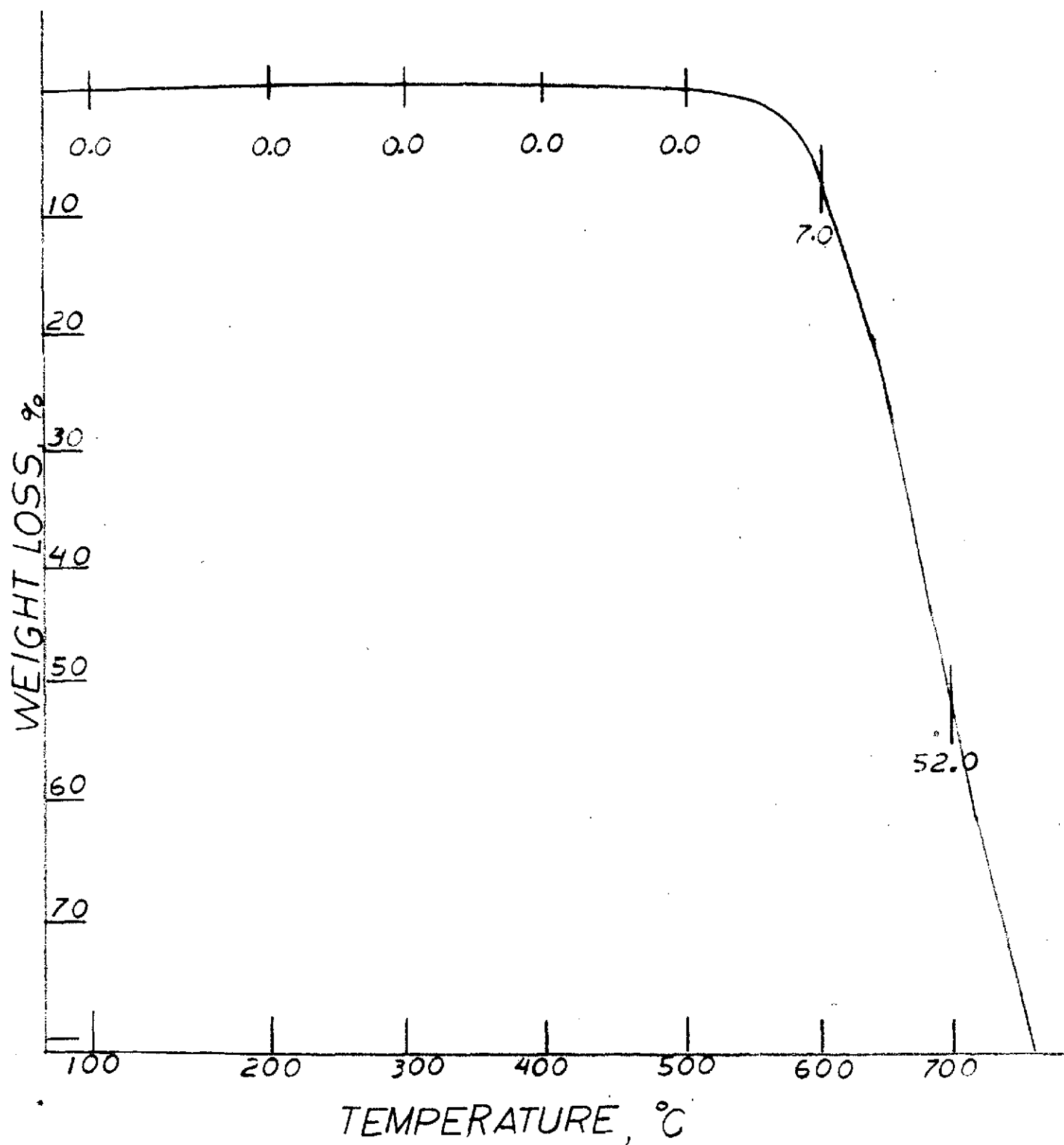


Figure 35. Thermogram of P100D100 in Air.

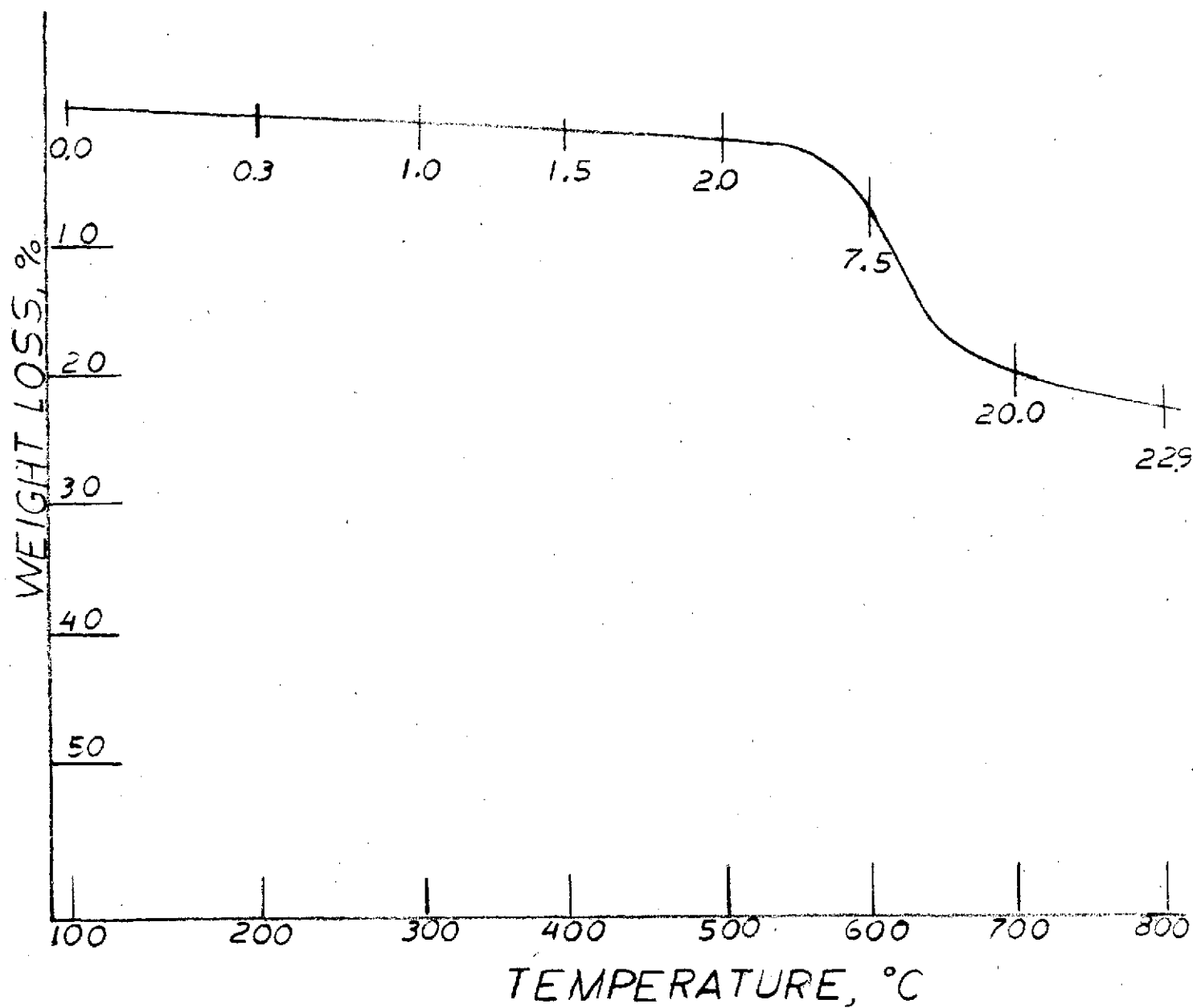


Figure 36. Thermogram of N100D95T5 in Helium.

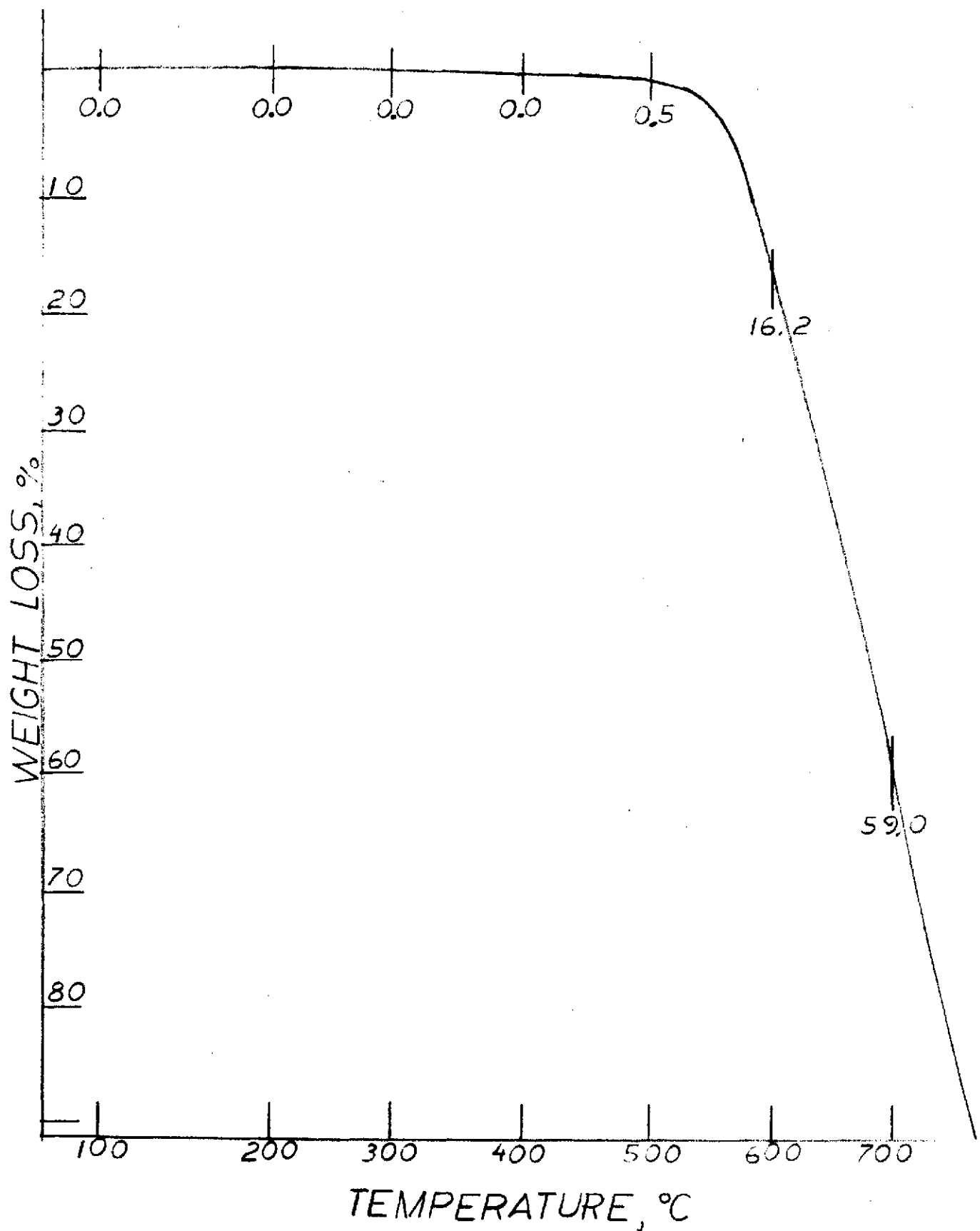


Figure 37. Thermogram of N100D95T5 in Air.

6. Isothermal Weight Loss

Table VI lists the percent weight loss of samples of the polyquinoxalines exposed at 304 - 321°C and at 357 - 371°C for 500 hours. In the 304 - 321°C environment, the homopolymer, P100D100 showed good oxidative resistance and the copolymers with the greater phenyl content showed greater oxidative resistance. In the 357 - 371°C regime, all the polymers were essentially oxidized. However, see Section III C 9 for the effect of tensile loading at elevated temperatures.

7. Solubility

All the freshly-prepared quinoxaline polymers were soluble in o-dichlorobenzene, chloroform, sym-tetrachloroethane and m-cresol. N100D100, N75P25D100 and N100D95T5 dissolved slowly in hot N-methylpyrrolidone and remained soluble when the solution was cooled; the other polymers were insoluble in this solvent. All the quinoxaline polymers prepared were insoluble both in cold and hot dimethylformamide, dimethylacetamide, carbon tetrachloride, dimethylsulfoxide and xylene. N100D100 and P100D100 were insoluble in cold and hot tetrahydrofuran, nitromethane and o-nitroanisole. After the polymer films had been heated to 371.1°C (700°F) (cf. Section III B 1, second procedure), they were almost entirely insoluble in all solvents tested.

8. Tensile Properties

The tensile properties at 204.4°C (400°F) and 315.6°C (600°F) of the quinoxaline polymers prepared are listed in Table VII.

9. Rupture under Sustained Tensile Loading

Table VIII lists the time to rupture of the quinoxaline polymers under sustained loading at elevated temperatures. At 204.4°C (400°F) and stressing at approximately 75% of the ultimate stress, no failure occurred in the approximately 100 hours of test and specimen weight loss was negligible. In an earlier test on N100D100 (preparation by first procedure, Section III B 1), failure occurred in 30 minutes at a loading of 75% of the ultimate stress at 204.4°C (400°F). It is believed that this early failure was

TABLE VI

PERCENT WEIGHT LOSS OF QUINOXALINE POLYMERS EXPOSED AT HIGH TEMPERATURES

Time Hrs	N100D100	N75P25D100	N50P50D100	N25P75D100	P100D100	N100D95T5
	At 304.4 - 321.1°C (580 - 610°F)					
146	21.3	14.6	12.6	9.0	3.7	5.5
244	45.6	57.6	31.9	24.9	5.5	20.1
356	80.2	94.0	75.1	73.4	7.7	59.8
500	93.5	99.1	92.1	92.5	18.4	82.1
	At 357.2 - 371.1°C (675 - 700°F)					
146	88.2	99.5	87.4	97.3	39.0	71.1
244	99.3	100	100	100	70.8	96.0
356	99.6	100	100	100	95.8	99.7
500	99.7	100	100	100	99.0	100

TABLE VII
TENSILE PROPERTIES OF SOME QUINOXALINE POLYMERS

	N100D100 ^a	N100D100 ^b	N75P25D100	N50P50D100	N25P75D100	P100D100	N100D95T5
<u>204.4°C (400°F)</u>							
Ultimate Strength, newtons/m ² x 10 ⁻⁶ (psi)	49.17 (7130)	63.24 (9170)	59.72 (8660)	57.87 (8390)	61.31 (8890)	70.34 (10,200)	57.52 (8340)
Total Strain to Failure, %	7.4	10	10	30	28	43	1
<u>315.6°C (600°F)</u>							
Yield Point newtons/m ² x 10 ⁻⁶ (psi)	18.41 (2670)	32.34 (4690)	31.72 (4600)	24.48 (3550 ^c)	32.14 (4660)	33.52 (4860)	27.65 (4010)
Ultimate Strength, newtons/m ² x 10 ⁻⁶ (psi)	18.41 (2670)	32.34 (4690)	31.72 (4600)	26.76 (3880 ^c)	37.59 (5450)	36.00 (5220)	27.65 (4010)
Total Strain to Failure, %	23.3	20	55	80	48	60	6

^a Prepared by the first procedure, Section III B 1

^b Prepared by the second procedure, Section III B 1

^c At 321.1°C (610°F)

due to inadequate heating of the specimen during its preparation either because incomplete removal of solvent had occurred or because of incomplete reaction. It is of significance that the ultimate tensile strengths at 204.4°C (400°F) and 315.6°C (600°F) of N100D100 prepared by the first procedure described in Section IIIB1 are markedly lower than when prepared by the second procedure.

The low weight changes observed (Table VIII) during the exposure under stress at 315.6°C are unexpected and are not consistent with the isothermal weight loss studies (Table VI) with unstressed materials. The ability of some polymer specimens to withstand loading at approximately 100% of the indicated ultimate stress is probably due to the variation of their tensile properties through a range. It is likely, however, that the samples were stressed to at least 90% of their ultimate stress.

TABLE VIII
TIME TO RUPTURE OF QUINOXALINE POLYMERS
UNDER SUSTAINED LOADING

	N100D100 ^a	N75P25D100	N50P50D100 ^b	N25P75D100	P100D100	N100D95T5
<u>204.4°C (400°F)</u>						
Tensile Load, newtons/m ² x 10 ⁻⁶ (psi)	47.17 (6840)	49.79 (7220)	42.21 (6120)	45.03 (6530)	53.72 (7790)	42.69 (6190)
Tensile Load, % of Ultimate Stress	75	83	73	73	76	74
Time of Test, hrs	101	117	98	138	114	95
Weight Change, %	+0.4 No Failure	-0.1 No Failure	+0.1 No Failure	-0.1 No Failure	+0.1 No Failure	-0.2 No Failure
<u>315.6°C (600°F)</u>						
Tensile Load, newtons/m ² x 10 ⁻⁶ (psi)	16.17 (2345)	15.93 (2310)	28.28 (4100)	18.90 (2740)	18.63 (2614)	13.83 (2005)
Tensile Load, % of Ultimate Stress	50 ^c	50 ^d	106	50	50	50 ^e
Time of Test, hrs	86	117	110	100	100	109
Weight Change, %	-0.51 Failed at Grip	-0.35 No Failure	-0.1 No Failure	-0.34 No Failure	+0.19 No Failure	-0.49 No Failure

NOTES TO TABLE VIII

- a. Prepared by second procedure, Section III B 1
- b. Prepared by second procedure, Section III B 3
- c. Samples stressed at 99% and 98% of the indicated ultimate stress failed at 1.4 and 40.1 hours respectively
- d. A sample stressed at 94% of the indicated ultimate stress failed at 1.9 hours
- e. A sample stressed at 104% of the indicated ultimate stress failed at 1.3 hours

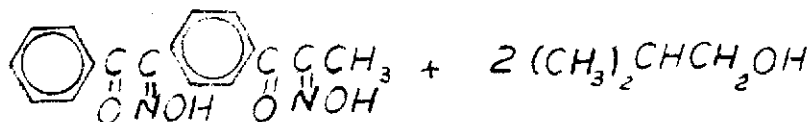
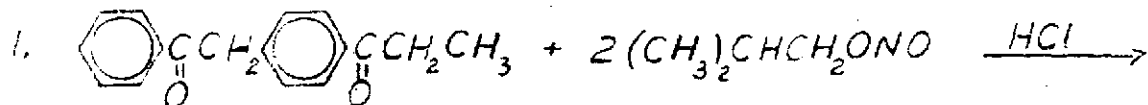
IV. CONCLUSIONS AND RECOMMENDATIONS

1. A method was devised for synthesizing 1,4-bis[(1'-naphthalenyl)-acetyl]benzene, a new intermediate chemical for the preparation of polynaphthalenylquinoxalines (PNQs), the analogs of the polyphenylquinoxalines (PPQs). Since the yield was good (60 - 70% of pure product), the procedure may be valuable as a general method for synthesizing bis(arylacetyl)benzene analogs useful as intermediates for the preparation of monomers for polyarylquinoxalines.
2. The preparation of some PNQs in solution may find use in the in situ polymerization-of-monomers technique of fiber-reinforced composite fabrication. The rate of reaction of the naphthalene monomer is so slow at room temperature that for practical purposes, polymerization may be considered not to occur. Therefore, it should be possible to B-stage the fibers which are impregnated with the solution of monomers to some desired tack at an elevated temperature, and then to complete polymerization during final cure at a higher temperature. This would not be possible with some PPQs because the monomers react rapidly at room temperature. It is recommended that the PNQs be used in the preparation of a graphite fiber-reinforced composite and that the mechanical properties of the composite be measured.
3. Model reactions using 2-methyl-3-phenylquinoxaline and N-phenylmaleimide indicated that cross-linking poly[2,2'-(1,4-phenylene)-3-phenyl-3'-methyl-6,6'-bisquinoxaliny] by reaction with 1,4-phenylenedimaleimide will probably occur. It is recommended that the preparation of the monomer necessary for this reaction, p-(methyloxalyl)benzil, be continued. It is recommended, further, that the preparation of polyquinoxalines having capability for cross-linking by addition polymerization be investigated.
4. Second-order phase transition temperatures of the PPQs and the PNQs did not differ appreciably. This suggests that the high-temperature plasticity of the polymers might be about the same. Creep measurements on composites are needed to evaluate this point.
5. It is possible that large planar bridging groups at the 2,2'-linkage or bulky groups at the 6,6'-linkage or two-stage cross-linking would accomplish the desired chain-stiffening in polyquinoxalines needed to reduce high-temperature plasticity. It is recommended, therefore, that monomers such as the bis-(aryloxalyl)naphthylidines [e.g., 1,5-bis(phenyloxalyl)naphthalene] be used to introduce chain-stiffening in polyquinoxalines.

V. APPENDICES

APPENDIX 1

Attempted Synthesis of 1,4-Bis[(1'-naphthalenyl)acetyl]benzene by Reaction between Di(1-naphthalenylmethyl)cadmium and Terephthaloyl chloride



(I)



The use of organo-cadmium compounds for the preparation of ketones from acid chlorides was first reported by Gilman and Nelson⁵³. The reaction was explored in detail by Cason⁵⁴. The organo-cadmium derivatives are said⁵⁵ to react with acid chlorides and anhydrides but are unreactive toward other functional groups. In the present instance, however, a mixture of 1,2-dinaphthalenylethane and unidentified products were obtained instead of the desired compound.

1-Naphthalenylmethylmagnesium chloride was prepared from 37.2 g (1.5 gram atoms) magnesium turnings and 88.3 g (0.5 mole) 1-(chloromethyl)naphthalene in ethyl ether. The solution of the Grignard compound was drained from the excess magnesium, and the yield was determined to be 86% by titration⁵⁶. Anhydrous cadmium chloride, 47.7 g (0.26 mole), was added to convert the Grignard reagent to bis(1-naphthalenylmethyl)cadmium. A solution of 36.5 g (0.18 moles) terephthaloyl chloride in anhydrous ether was added at a rate such that the exothermic reaction produced a rapid reflux. After 1 1/2 hours of reaction, the mixture was filtered. The filtrate was evaporated yielding 15 g of a residue (fraction 1081-94-1). The residue was extracted with three portions of boiling benzene totalling one

liter (1081-94-2). The residue was extracted with water, filtered and dried (1081-94-3). Fraction 1081-94-1, 15 g was extracted with 30 cc methylene chloride and filtered yielding 4.5 g of compound 1081-94-1-1. The filtrate was evaporated to dryness yielding 10.2 g of compound 1081-94-1-2. A portion of 1081-94-1-1 was recrystallized from chloroform yielding 1081-94-1-1-1 melting at $162 - 3^{\circ}\text{C}$. 1,2-Bis(1'-naphthalenyl)ethane melts at $162 - 3^{\circ}\text{C}$ ⁵⁷. The infrared spectrum of 1081-94-1-1-1 is shown in Figure 38 and is consistent with an assignment of 1,2-bis-(1'-naphthalenyl)ethane as its structure. Absorption associated with 1-naphthalenyl (Colthup Table) is present at 3050, 1590, 1500, 1400, 780 and 760 cm^{-1} ; comparable absorption is found in the spectra for 1-chloromethylnaphthalene (Figure 39). The absence of carbonyl absorption at $1650-1725\text{ cm}^{-1}$ definitely precludes the assignment of 1,4-bis(1'-naphthalenylacetyl)benzene to 1081-94-1-1-1.

A 0.69 g portion of 1081-94-1-2 was dissolved in 1 cc of boiling acetic acid. The solution was cooled and 0.08 g of 1081-94-1-2-1 was filtered off, washed with acetic acid and dried; it melted at $251 - 57^{\circ}\text{C}$ after darkening at 240°C . Unexpectedly, it was no longer sufficiently soluble in acetic acid to be recrystallized from this solvent. The infrared spectrum of this compound is shown in Figure 40; absorption associated with 1-naphthalenyl is observable. Absorption associated with carbonyl is present at 1690 cm^{-1} . The spectrum shown in Figure 40 differs extensively from Figure 1 (of the main text) and therefore, 1081-94-1-2-1 is not 1,4-bis[(1'-naphthalenyl)acetyl]benzene. Furthermore, 1081-94-1-2-1 failed to form a 2,4-dinitrophenylhydrazone. No further attempts at identification were made.

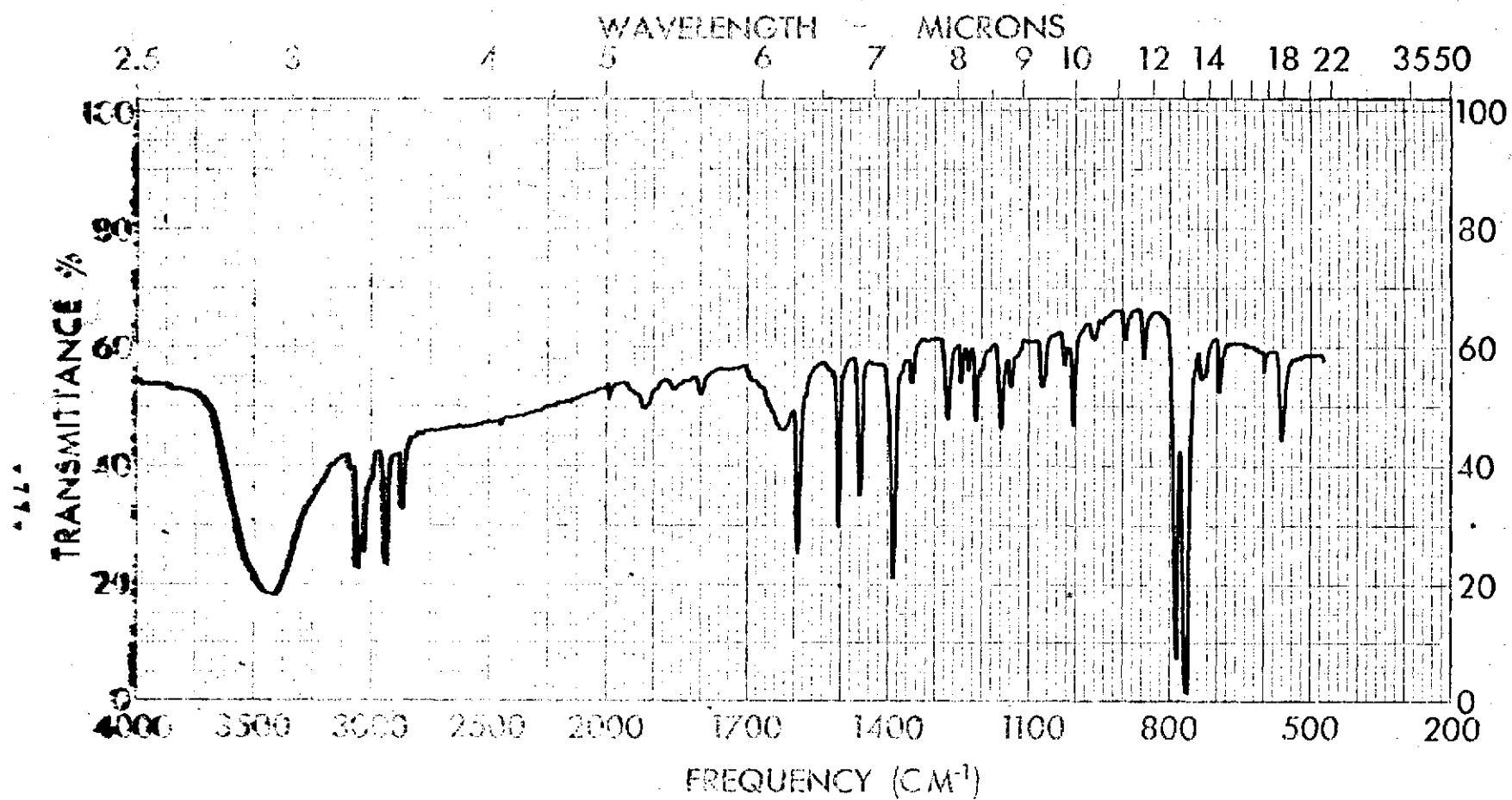


Figure 38. Infrared Spectrum of 1,2-Bis(1'-naphthalenyl)ethane (Compound 1081-94-1-1-1).

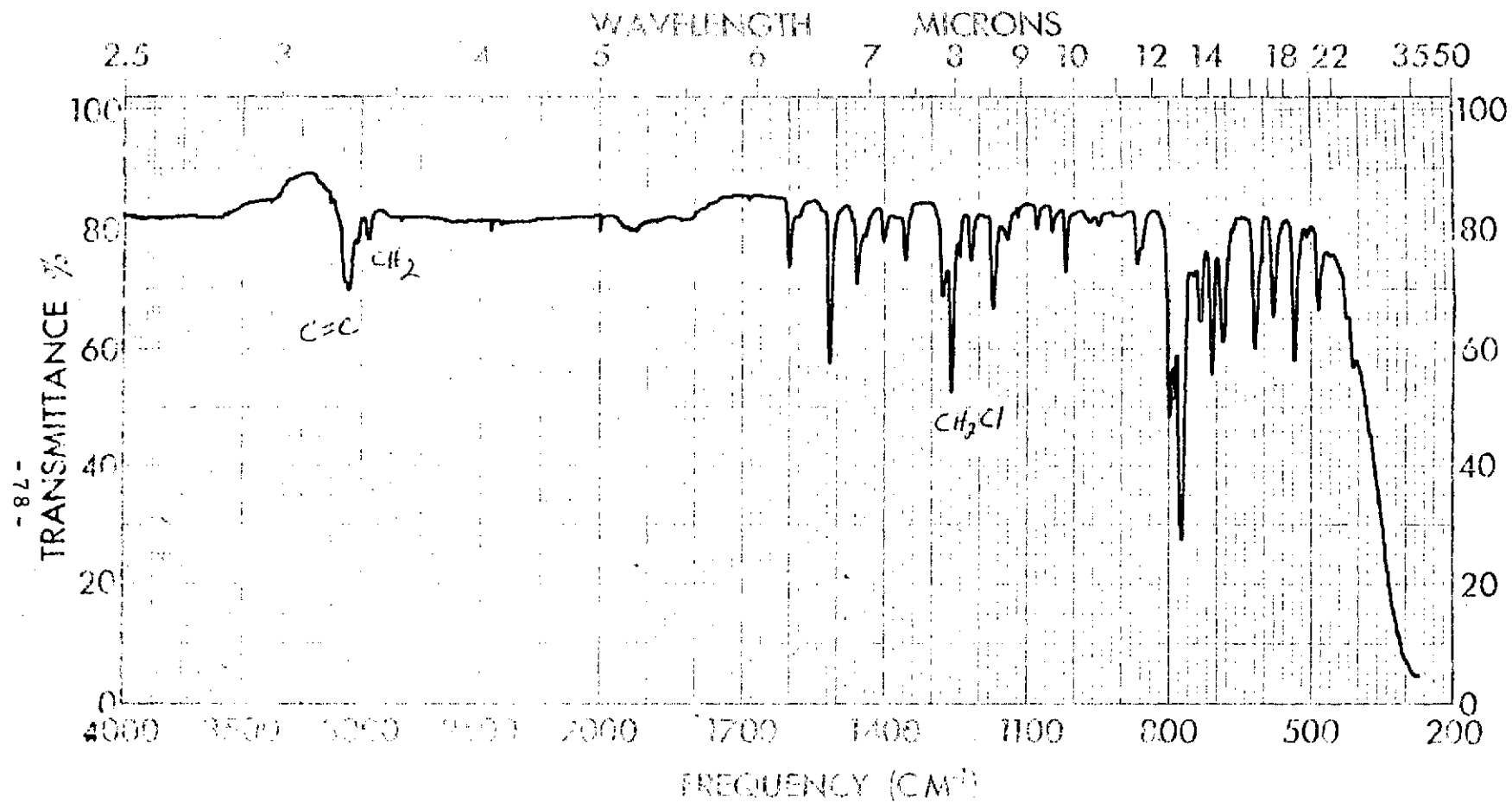


Figure 39. Infrared Spectrum of 1-Chloromethylnaphthalene.

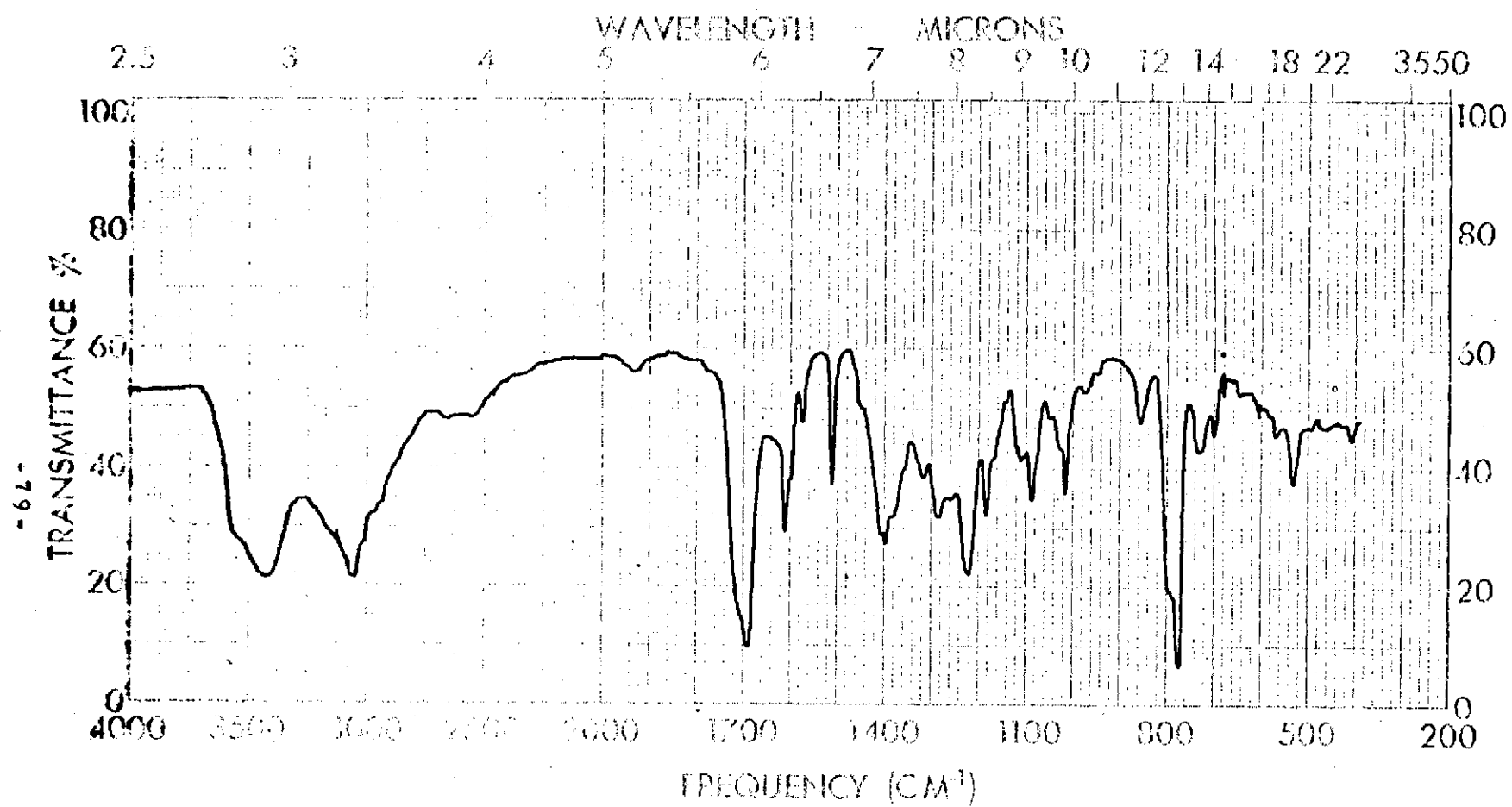
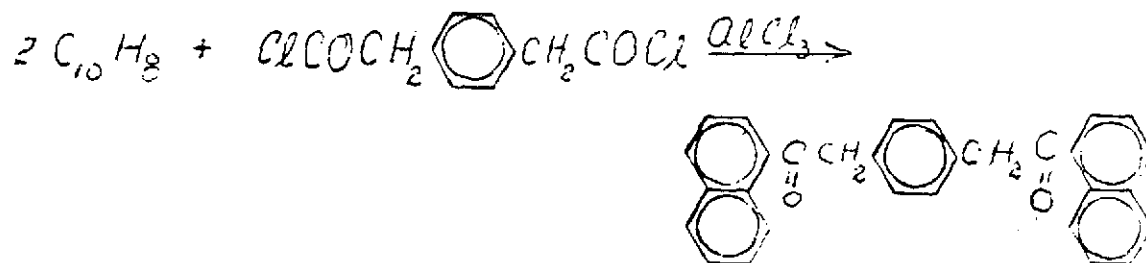


Figure 40. Infrared Spectrum of Compound 1081-94-1-2-1.

APPENDIX 2

Attempted Preparation of 1,4-Di(1'-naphthalenylcarbonyl)phenylene-methylene by the Friedel-Crafts Reaction between Naphthalene and 1,4-Phenylenedi(acetyl chloride)

The approach that Wrasidlo and Augl⁸ used to prepare the bis-(phenyloxalyl)benzenes was adapted to an attempted preparation of 1,4-bis[(1'-naphthalenyl)oxalyl]benzene. Ethylene chloride was used as the solvent instead of benzene (which served as the solvent as well as the reactant for Wrasidlo and Augl) because ethylene chloride has produced high yields of α -substitution in Friedel-Crafts reactions with naphthalene⁵⁸.



A solution of 55.9 g (0.242 mole) p-phenylenediacetyl chloride in 250 ml ethylene chloride was slowly added, during a 35 minute period, to a stirred mixture of 70.3 g (0.548 mole) naphthalene, 87.7 g (0.658 mole) aluminum chloride and 250 ml ethylene chloride. The initial exothermic reaction was controlled by cooling with an ice-bath. The reaction mixture was poured into 300 g concentrated hydrochloric acid and 700 g crushed ice. The ethylene chloride layer was separated, extracted with water and the aqueous extract was discarded. When the ethylene chloride phase was evaporated to dryness, a gummy residue was obtained. Attempts at crystallization of the residue were unsuccessful, but it was converted to 87 g of a yellow powder, 1206-124-1 (m. p. 155- > 285°C) by extraction with a solution of 360 ml heptane and 40 ml chloroform. A gas chromatographic analysis (Figure 41) of the powder showed it to be a complex mixture. Attempts to distill the powder at 10 μ were unsuccessful; decomposition set in at a pot temperature of about 250°C.

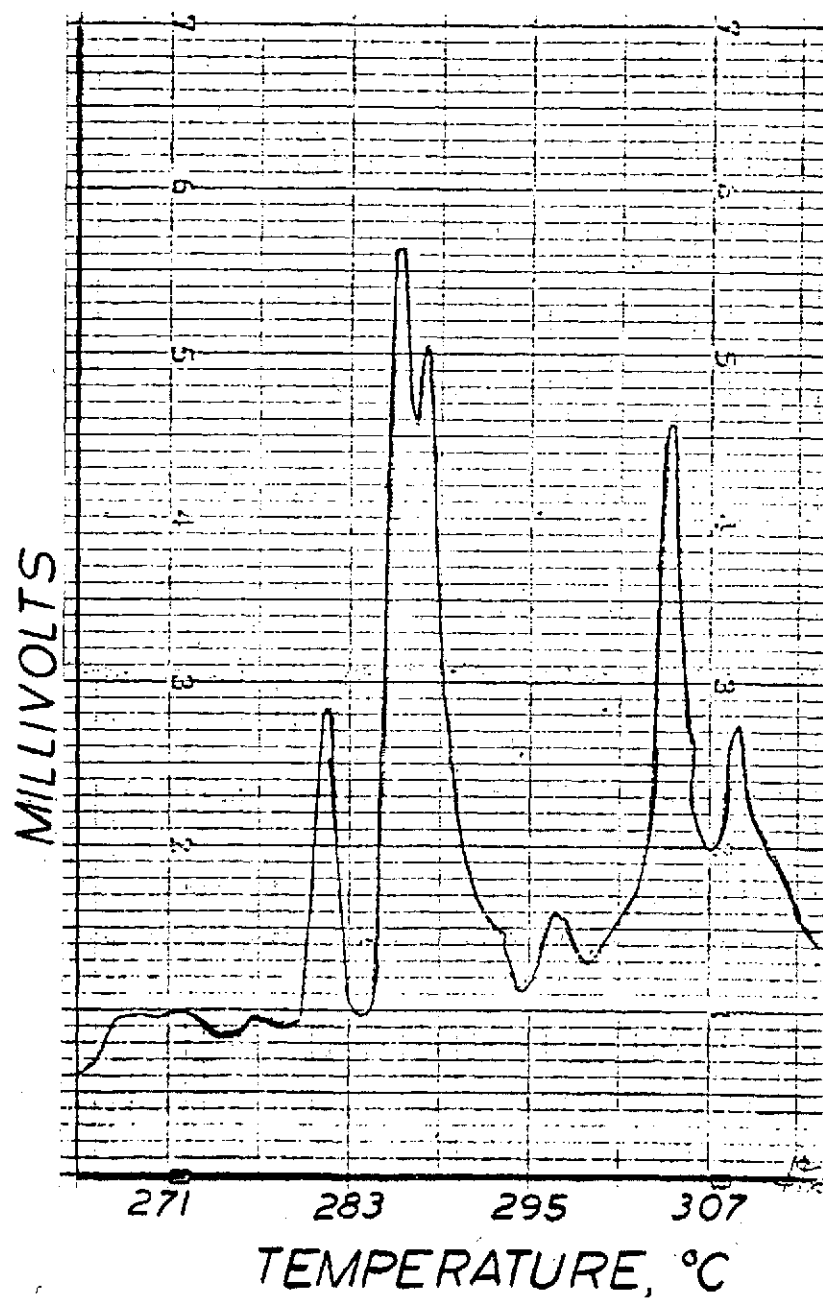


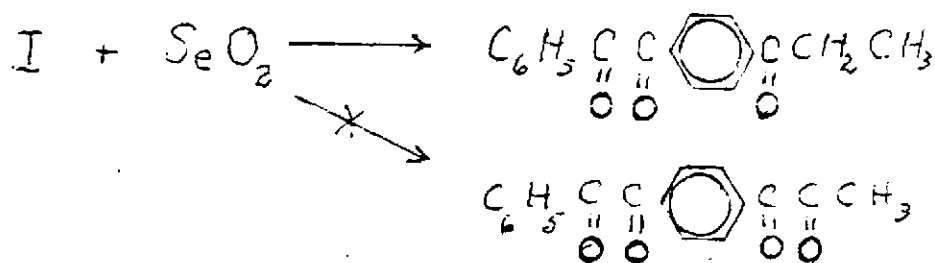
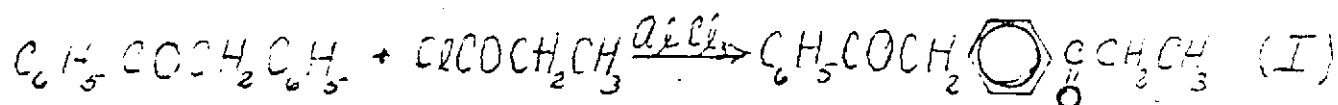
Figure 41. Gas Chromatogram of Friedel-Crafts Reaction Product (Compound 1206-124-1).

APPENDIX 3

Attempted Preparation of p-(Methyloxalyl)benzil

1. By Oxidation of p-Phenacylpropiophenone

It was planned to prepare p-phenacylpropiophenone and to oxidize this compound to p-(methyloxalyl)benzil. p-Phenacylpropiophenone was prepared by the Friedel-Crafts reaction between deoxybenzoin and propionyl chloride. Oxidation of p-phenacylpropiophenone by selenium dioxide gave p-(phenyloxalyl)propiophenone instead of the desired p-(methyloxalyl)benzil.



This result was unexpected in view of Riley and Gray's⁵⁹ preparation of phenylglyoxal in good yield by oxidation of acetophenone with selenium dioxide and Fuson's⁶⁰ oxidation of propiophenone with selenium dioxide to methyl phenyl diketone in 50% yield.

a. Preparation of p-Phenacylpropiophenone

A solution of 68.6 g (0.35 mole) of deoxybenzoin and 33.4 g (0.35 mole) propionyl chloride in 200 ml carbon disulfide was slowly added with mechanical stirring to a mixture of 116.9 g (0.88 mole) aluminum chloride suspended in 200 ml of carbon disulfide. A slow increase in temperature was observed which reached a maximum of 40°C; slight fuming occurred at this temperature. The stirred mixture was then heated to the reflux

point (41°C) for 3 days. The mixture was cooled to room temperature and was poured into 300 g concentrated hydrochloric acid and 700 g crushed ice. The carbon disulfide was removed by evaporation and a crude separation of the residual organic phase (a mixture of crystals and a liquid) was made by decanting off the aqueous phase. The organic phase was extracted with 200 ml benzene and the crystals of p-phenacylpropiophenone were filtered off, washed with 200 ml benzene and dried. The yield was 24.4 g (27.7%). The crude product was recrystallized from 300 ml benzene yielding 14 g white plates m.p. 139-140.5°C. Additional crops of crystals were obtained on concentration (5.6 g). To establish the identity of the compound, an infrared spectrum was prepared (Figure 42) and compared with infrared spectra for deoxybenzoin and propiophenone. Table IX compares the absorption bands of the three compounds. The absorption data indicates that the compound prepared is a para-substituted benzene derivative containing -CH₃ and -CH₂C=O groups. These findings are consistent with p-phenacylpropiophenone.

From the benzene extract, 55 g of a dark brown residue was obtained when the solvent was evaporated. This was fractionally distilled, and a 6.4 g fraction boiling at 178-185°C at 50-70 μ was shown by infrared spectrophotometry to be p-phenacylpropiophenone.

b. Oxidation of p-Phenacylpropiophenone

A mixture of 13.9 g (0.055 mole) p-phenacylpropiophenone and 15.6 g (0.141 mole) selenium dioxide in 115 ml acetic anhydride was refluxed for 3 1/2 hours during which time the mixture became dark red. The mixture was filtered hot, cooled and treated with 115 ml distilled water. A brown precipitate formed which changed to a black oil. When the mixture was cooled in ice, orange crystals formed. The crystals, oil and aqueous filtrate were separated into an aqueous phase (discarded), an oil (8.0 g, sample number 1206-71-3) and orange crystals (2.1 g, 1206-71-1). Recrystallization of a portion of 1206-71-1 from hexane gave yellow crystals (1206-71-4) which melted from 70 to 120°C indicating a mixture was present. Recrystallization of 1.7 g, 1206-71-1 from 25 ml of benzene and 50 ml of hexane gave crystals melting in the range 127-136°C (1206-73-3) which on crystallization from ethanol gave crystals, m.p. 137-138.5°C (1206-79-2), whose infrared spectrum is shown in Figure 43. The filtrate from 1206-73-3 was evaporated to dryness giving a residue (1206-73-4), m.p. 68-72°C, which when recrystallized from hexane gave sample number 1206-73-5, m.p. 75-75.7°C, whose infrared spectrum is shown in Figure 44.

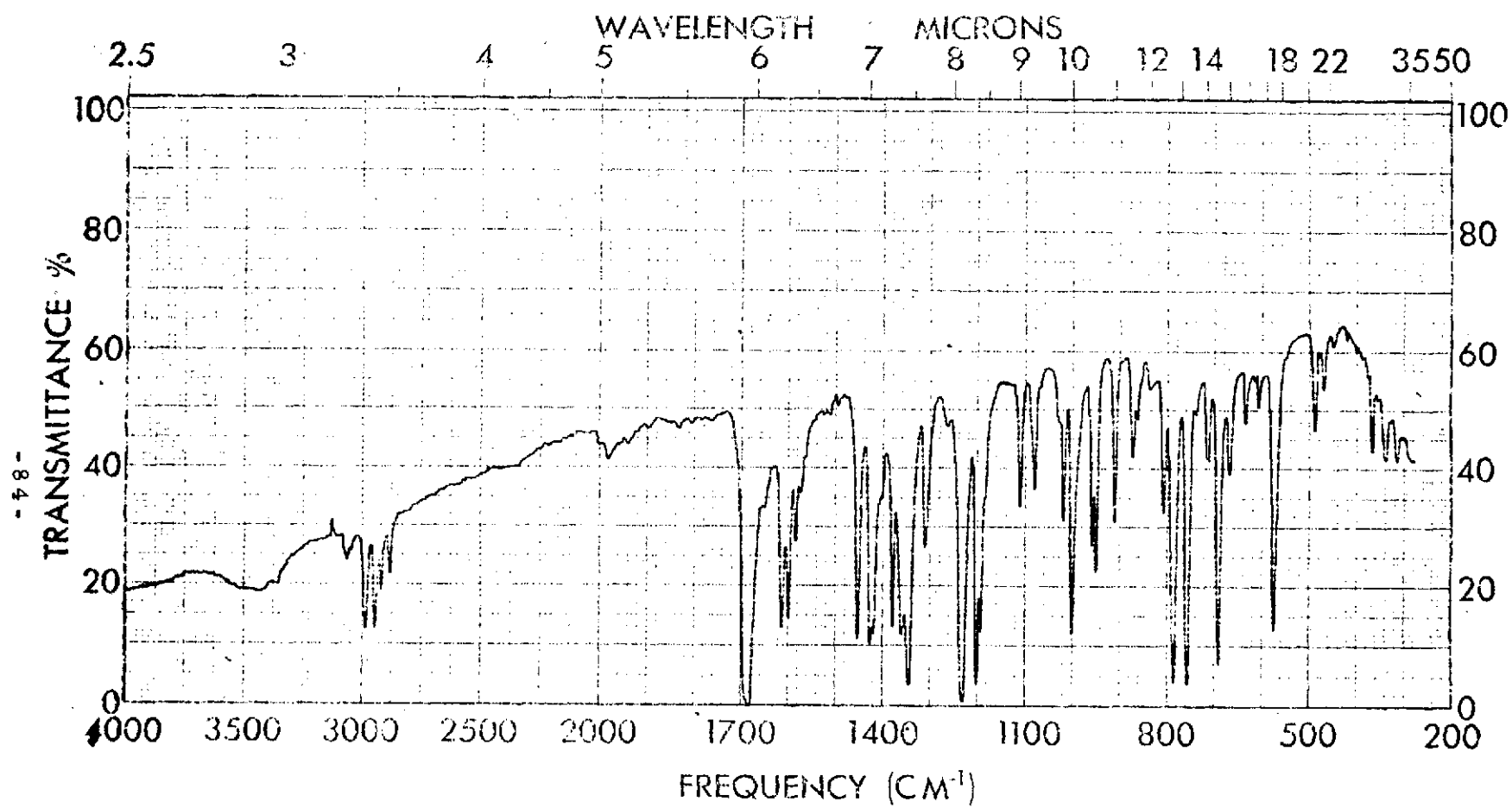


Figure 42. Infrared Spectrum of p-Phenacylpropiophenone.

TABLE IX

 IDENTIFICATION OF SYNTHESIZED COMPOUND AS
 p-PHENACYLPROPIOPHENONE FROM INFRARED ABSORPTION CHARACTERISTICS

Structure	(1)		Propiophenone	Desoxybenzoin	p-Phenacyl- propiophenone
	Absorption	Frequency cm ⁻¹			
CH ₃ C	3000-2900	s	present	absent	present
	2950-2830	s	present	absent	present
	1480-1430	s	present	1445	1450
	1400-1350		present	absent	1360
CH ₂ (C=O)	3050-2925		present	present	present
	2975-2880		present	present	present
	1440-1390		present	present	present
Aromatic Ketone	1725-1650	s	1680	1680	1680
	1375-1210	m	1350	1335 (1210)	1305
Monosubstituted benzene	3000-3050	m			
	1640-1560	m	1600, 1580 doublet	1595, 1575 doublet	1615, 1600 doublet
	1180-1130	w	1180	1160	1110
	1110-1060	w	1075	1075	1080
	1060-1020	w	1020	1020	1020
Parasubstituted benzene	1650-1560		absent	absent	1580 m
	1280-1175				
	1130-1100				
	1060-1000				
	860-800	s	absent	absent	810 s
	575-450	w			490 m

(1) Data taken from Correlation Tables N.B. Colthup "Application of Absorption Spectroscopy of Organic Compounds" quoted in Cook and Jones, "A Programmed Introduction to Infrared Spectroscopy". s=strong, m=moderate, w=weak

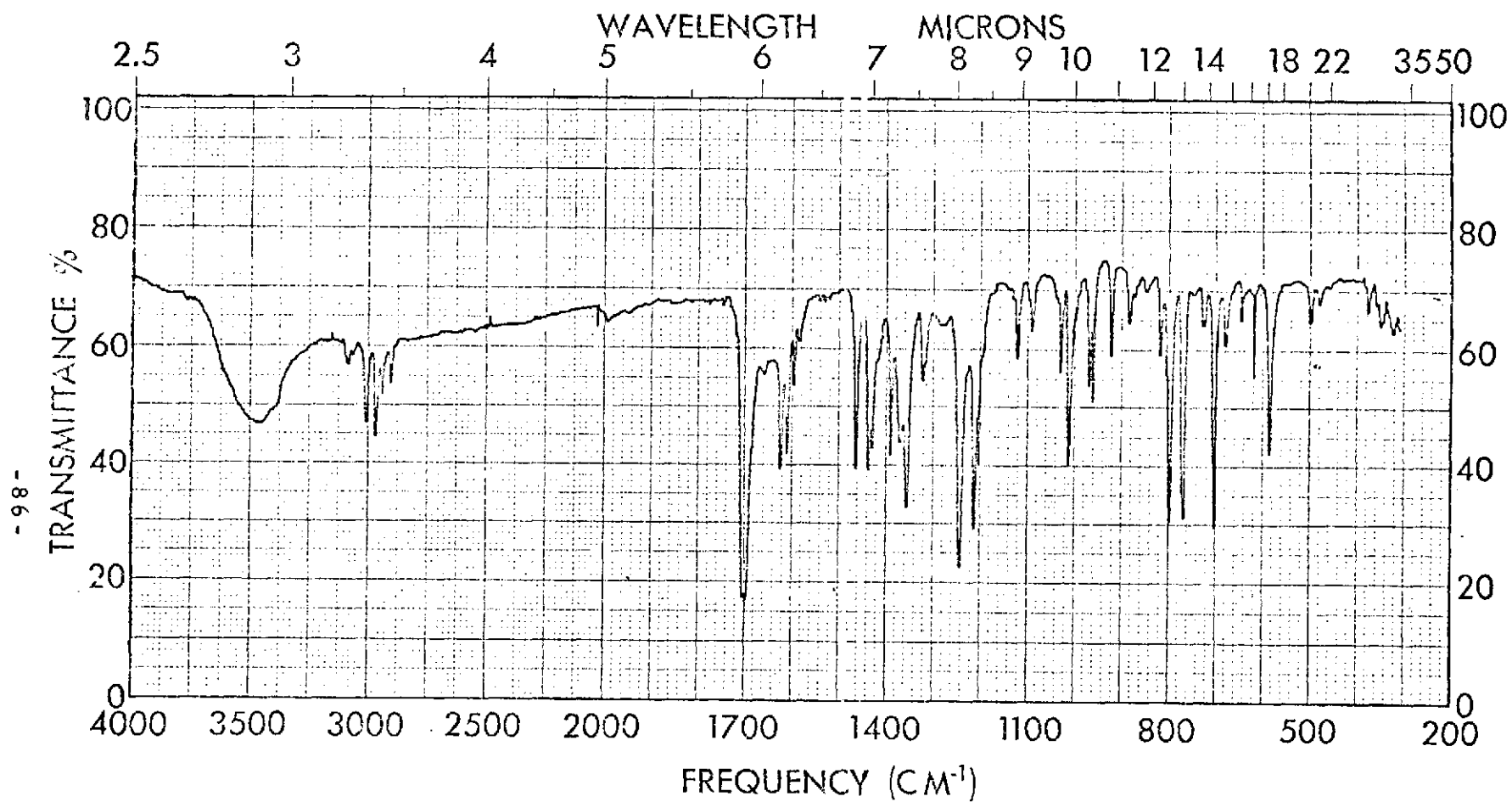


Figure 43. Infrared Spectrum of Compound 1206-79-2.

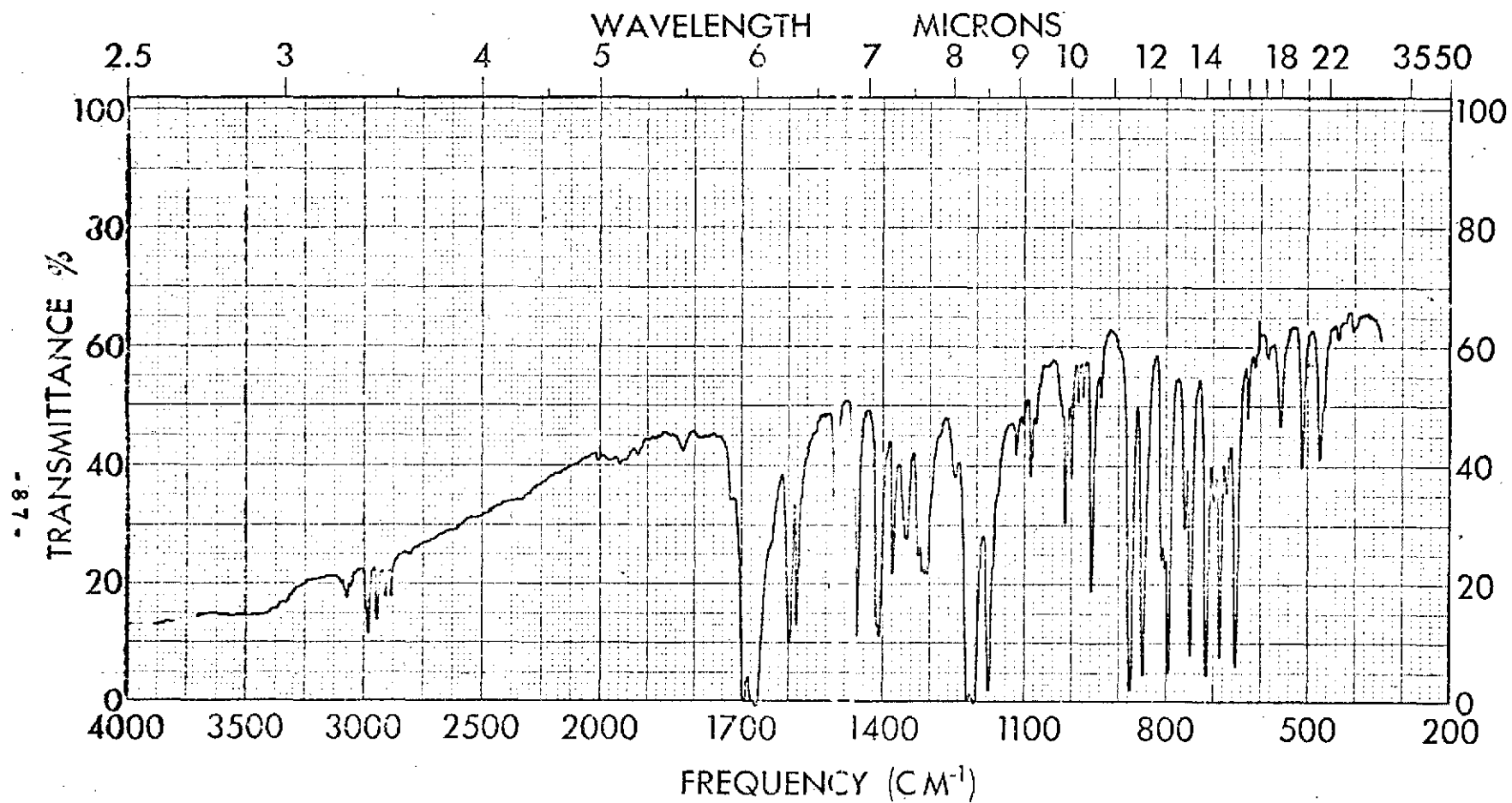


Figure 44. Infrared Spectrum of Compound 1206-73-5.

It was believed at first that 1206-73-5 was p-(methyloxalyl)-benzil, but the nuclear magnetic resonance (NMR) spectrum (Figure 45) of this compound shows that this could not be the case. The triplet at δ 1.32 and the quadruplet at δ ~2.9 form a typical ethyl pattern which eliminated p-(methyloxalyl)benzil as the structure for 1206-73-5 since this compound lacks an ethyl group. The multiplets at δ 8.0 and δ 7.5 are associated with the hydrogens of the phenyl rings. The absence of any other peaks excludes all other modes of hydrogen and thereby eliminates p-phenacylpropiophenone (the starting material). Since SeO_2 oxidation of $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{CH}_2\text{C}_6\text{H}_4-$ to $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{C}_6\text{H}_4-$ is known (e.g. Wrasidlo and Augl⁸, among others), designation of p-propionylbenzil as the structure for 1206-73-5 is most probable.

Figure 46 shows the NMR spectrum of 1206-79-2 in deuterated dimethylsulfoxide together with the NMR spectrum for the solvent (a). The NMR spectrum for 1206-79-2 shows that an ethyl group is present because of the triplet at δ 1.32 and the quadruplet at δ ~2.9. In addition to the multiplets at about δ 8.0 and δ 7.5 (attributable to the hydrogen in the phenyl ring), a singlet appears at δ 4.45 which is due to uncoupled methylene. These findings point to p-phenacylpropiophenone as a probable assignment for 1206-79-2. This is confirmed by a comparison of the infrared spectra for 1206-79-2 (Figure 43) and for known p-phenacylpropiophenone (Figure 42).

It is possible that the oil (sample 1206-71-3) contains p-(methyloxalyl)benzil; however, purification of the oil was not pursued.

2. By Hydrolysis of the Di-isonitroso Derivative of p-Phenacylpropiophenone

An alternate method for the preparation of p-(methyloxalyl)benzil entails the preparation and hydrolysis of the di-isonitroso derivative of p-phenacylpropiophenone:

- (a) The NMR spectrum for the solvent would not be observable at the amplitudes normally used. However, because the solute concentration was low, the amplitude was made unusually high, and a spectrum for the solvent was obtained which is due to the hydrogen-deuterium interchange.

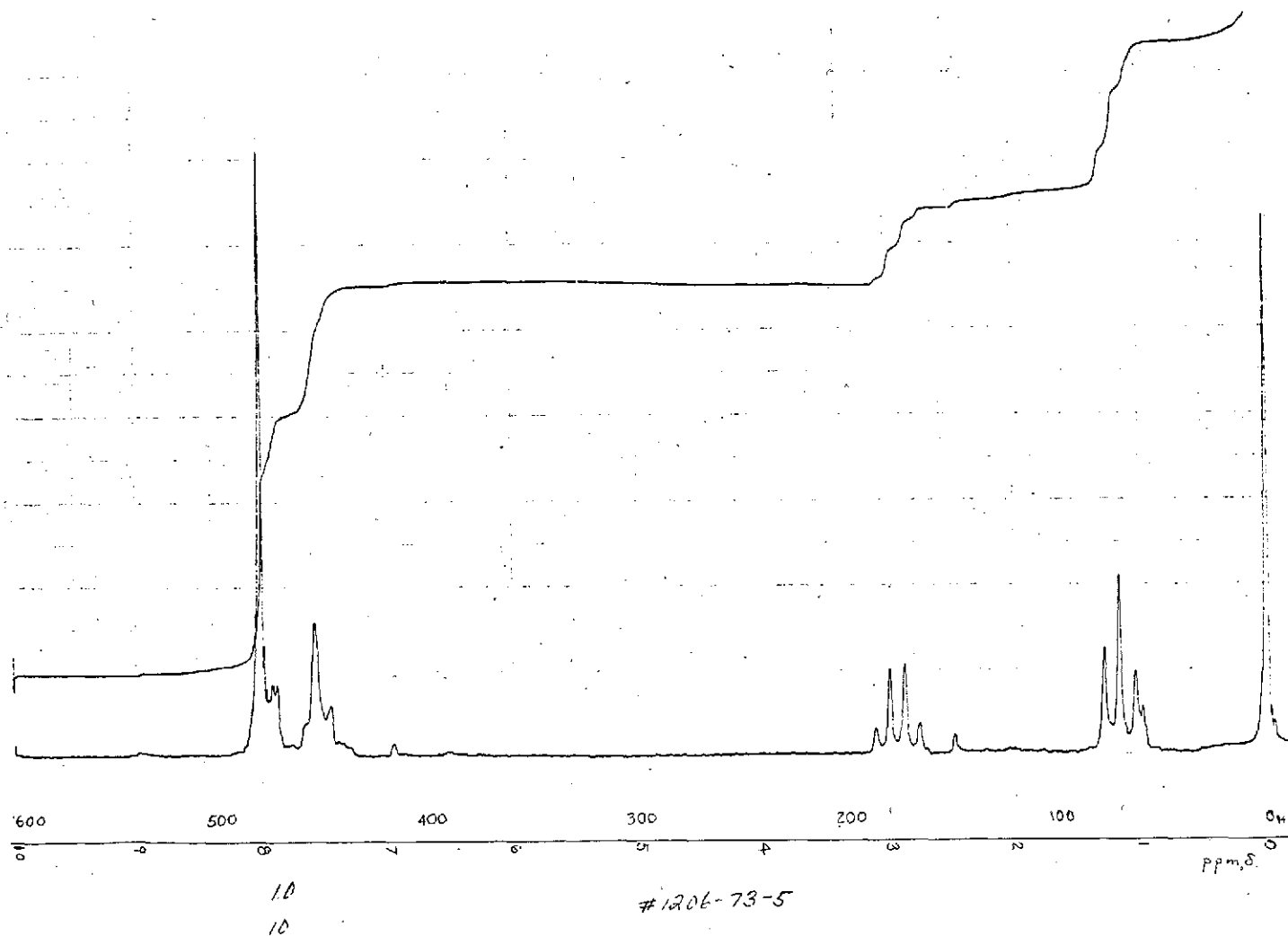


Figure 45. Nuclear Magnetic Resonance Spectrum of Compound 1206-73-5 (p-Propionylbenzil).

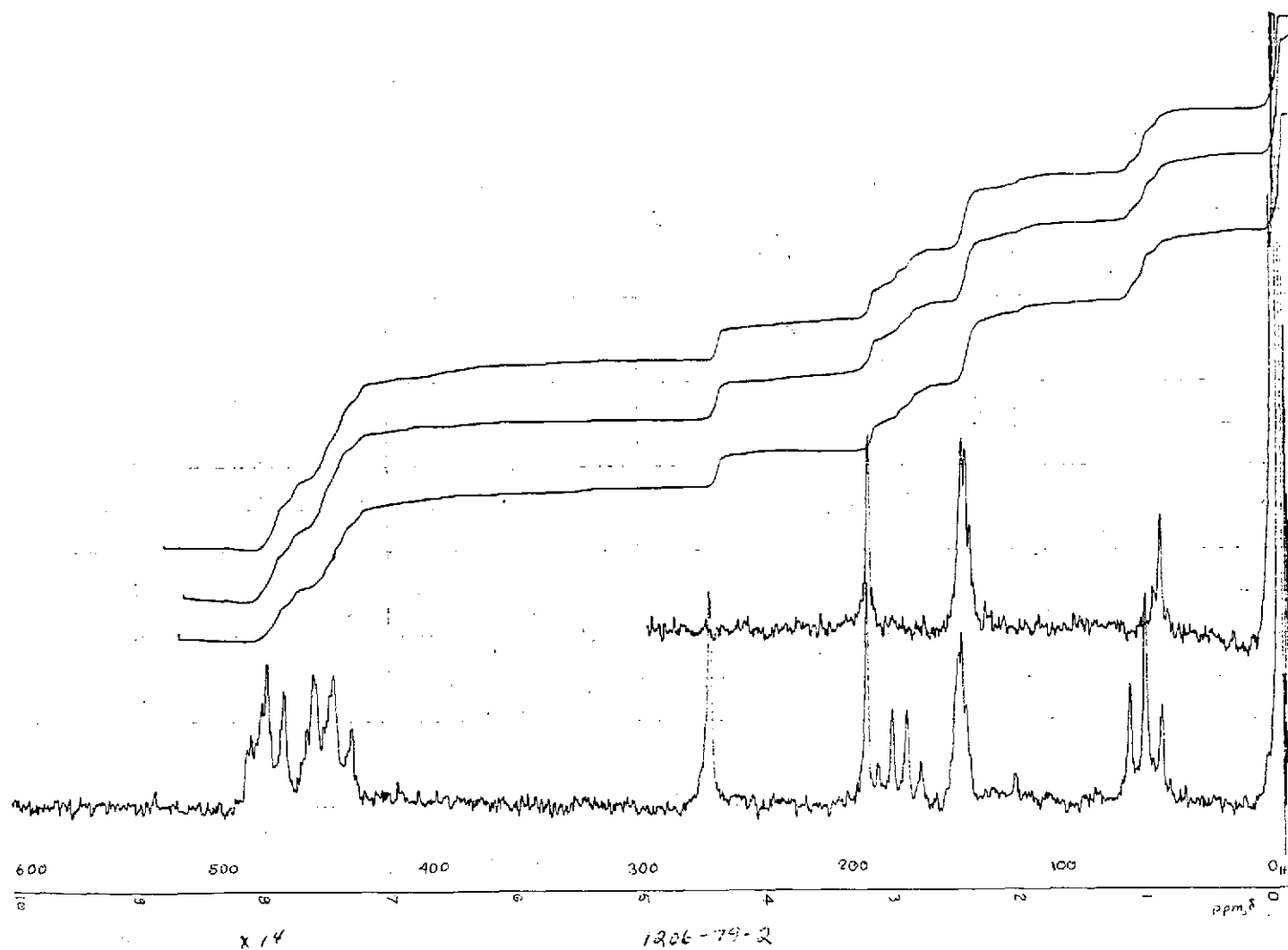
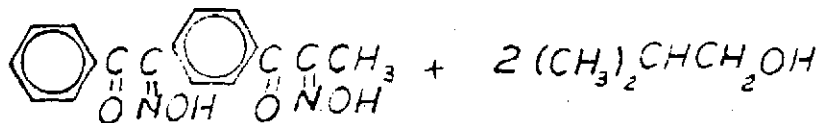
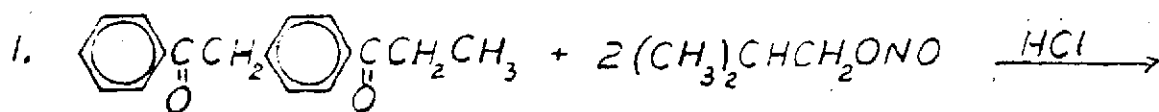


Figure 46. Nuclear Magnetic Resonance Spectrum of Compound 1206-79-2 in Deuterated Dimethylsulfoxide.



(I)



An analogous synthesis, preparation of isonitrosopropiophenone from propiophenone, is given by Hartung and Crossley⁶¹.

a. Preparation of 1-p-(1'-Phenyl-1'-oxo-2'-oximinoethyl)phenyl-1,2-propanedione-2-oxime

A solution of 6 g (0.051 mole) isoamyl nitrite in 25 ml methylene chloride was slowly added (80 minutes) to a solution of 5.5 g (0.022 mole) p-phenacylpropiophenone in 75 ml methylene chloride while a rapid stream of dry hydrogen chloride was bubbled through the solution. When the addition was complete, the solution was heated to the reflux point. After a total of three hours, the solution was cooled to room temperature. A compound (1206-112-1) crystallized from the solution and was filtered off, washed with methylene chloride and dried. The yield was 0.9 g, m.p. 181°C. On the following day, a second crop of crystals (1206-113-1) was obtained from the filtrate in 0.7 g yield. If the compound is assumed to be 1-p-(1'-phenyl-1'-oxo-2'-oximinoethyl)phenyl-1,2-propanedione-2-oxime, the yield was 24.5%. When 1206-113-1 was recrystallized from 50% ethyl alcohol/water, it was obtained as white platelets which melted at 182.5 - 4°C. An attempt was made to recover additional material from the methylene chloride filtrate by extraction with 10% sodium hydroxide solution and acidification of the aqueous extract with hydrochloric acid (in accordance with the method of Hartung and Crossley)⁶¹. A gummy material was obtained which was not further purified.

In an alternate method of preparation, methyl nitrite was substituted for amyl nitrite. A solution of 50.4 g (0.2 mole) of p-phenacylpropiophenone was dissolved in 300 ml methylene chloride. Methyl nitrite [generated by the dropwise addition of 60 ml 33% aqueous sulfuric acid to 35.6 g (0.5 mole) sodium nitrite suspended in 18 g (0.56 mole) methanol and 21.4 ml water] and dry hydrogen chloride were simultaneously bubbled into the methylene chloride solution. Two hours after the addition of methyl nitrite was begun, the reddish solution turned yellow and a precipitate formed. The addition of methyl nitrite and hydrogen chloride were continued until all the sodium nitrite had been consumed. The precipitate was filtered off and dried; the yield was 30.7 g (49.5% yield). The product melted at 180.3 - 181.5 °C; recrystallized from 95% ethyl alcohol, it melted at 189 - 189.5 °C with decomposition. A chemical analysis showed that the compound, contained 9.14% nitrogen; the theoretical nitrogen content of $C_{17}H_{14}N_2O_4$ is 9.03%.

b. Attempted Hydrolyses to p-(Methyloxalyl)benzil

Several techniques for hydrolysis of oximes to ketones have been reported, but in all cases a method for shifting the equilibrium: $\text{oxime} + \text{water} \rightleftharpoons \text{ketone} + \text{hydroxylamine}$ appears necessary. Hartmann and Roll⁶² hydrolyzed isonitrosopropiophenone with 10% sulfuric acid and shifted the equilibrium by steam-distilling the produced 1-phenyl-1,2-propanedione. Cava, Little and Napier⁶³, hydrolyzed 2-oximino-1-indanone to 1,2-indanedione in concentrated formaldehyde and hydrochloric acid shifting the equilibrium by forming the formaldoxime. Similarly, Depuy and Ponder⁶⁴, used levulinic acid and claimed high yields of the desired ketones. A fourth procedure involves oxidation of the generated hydroxylamine. Bezzi⁶⁵ used acid hydrolysis and simultaneous ferric chloride oxidation of both mono-oximes of benzoylacetyl to obtain benzoylacetyl in high yield.

Procedures involving acidic hydrolysis and formation of a new oxime and oxidative methods were used in attempted hydrolyses of 1-p-(1'-phenyl-1'-oxo-2'-oximinoethyl)phenyl-1,2-propanedione-2-oxime (1206-112-1) to p-(methyloxalyl)benzil.

(1) Methods Using Acidic Hydrolysis and New Oxime Formation

Hydrolysis of 1206-112-1 with concentrated hydrochloric acid gave only a gum. Hydrolysis of 0.4 g 1206-112-1 with 5 ml 37% formalin 3 drops concentrated hydrochloric acid and 25 ml acetone was carried out by refluxing the mixture for 24 hours and concentrating the mixture to 10 ml. The cooled residue was extracted with chloroform, the chloroform extract was washed successively with dilute alkali and water, and the neutral extract was dried. The extract was evaporated leaving a poor yield of a paste.

Similarly, hydrolysis of 1206-112-1 with levulinic acid and hydrochloric acid gave a poor yield of an oil.

(2) Oxidative Methods

(a) Ferric Chloride

A solution of 0.2 g 1-[p-(1'-phenyl-1'-oxo-2'-oximino-ethyl)phenyl]-1,2-propanedione-2-oxime in 2 ml ethanol was treated with 2 ml of a solution of 3 g concentrated H_2SO_4 and 13.6 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 30 ml water. The resulting solution was refluxed for 45 minutes and then cooled. An oil separated from the solution. The entire solution was extracted with 3 one-ml portions of methyl isobutyl ketone. The extracts were combined, washed with 3 one-ml portions of water and the solvent was evaporated to dryness on the steam bath. The resulting oil slowly crystallized giving 0.2 g of a dark brown product which was recrystallized from 3 ml ethanol and 1 ml water. The crystals which formed (1206-118-4) were filtered off and dried; they melted at 155 - 200°C.

A second attempt at hydrolysis was made using toluene as a solvent. A solution of 3.0 g 1206-112-1 in 60 ml toluene was treated with a solution of 3 g concentrated sulfuric acid and 13.6 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 60 g water. The mixture was stirred mechanically and refluxed for 24 hours and then cooled. The toluene layer was separated and evaporated to dryness leaving 3.1 g of a brown oil (1206-141-4). Attempts at crystallization of this oil proved unsuccessful. Gas chromatography (Figure 47) showed the presence of at least two principal components.

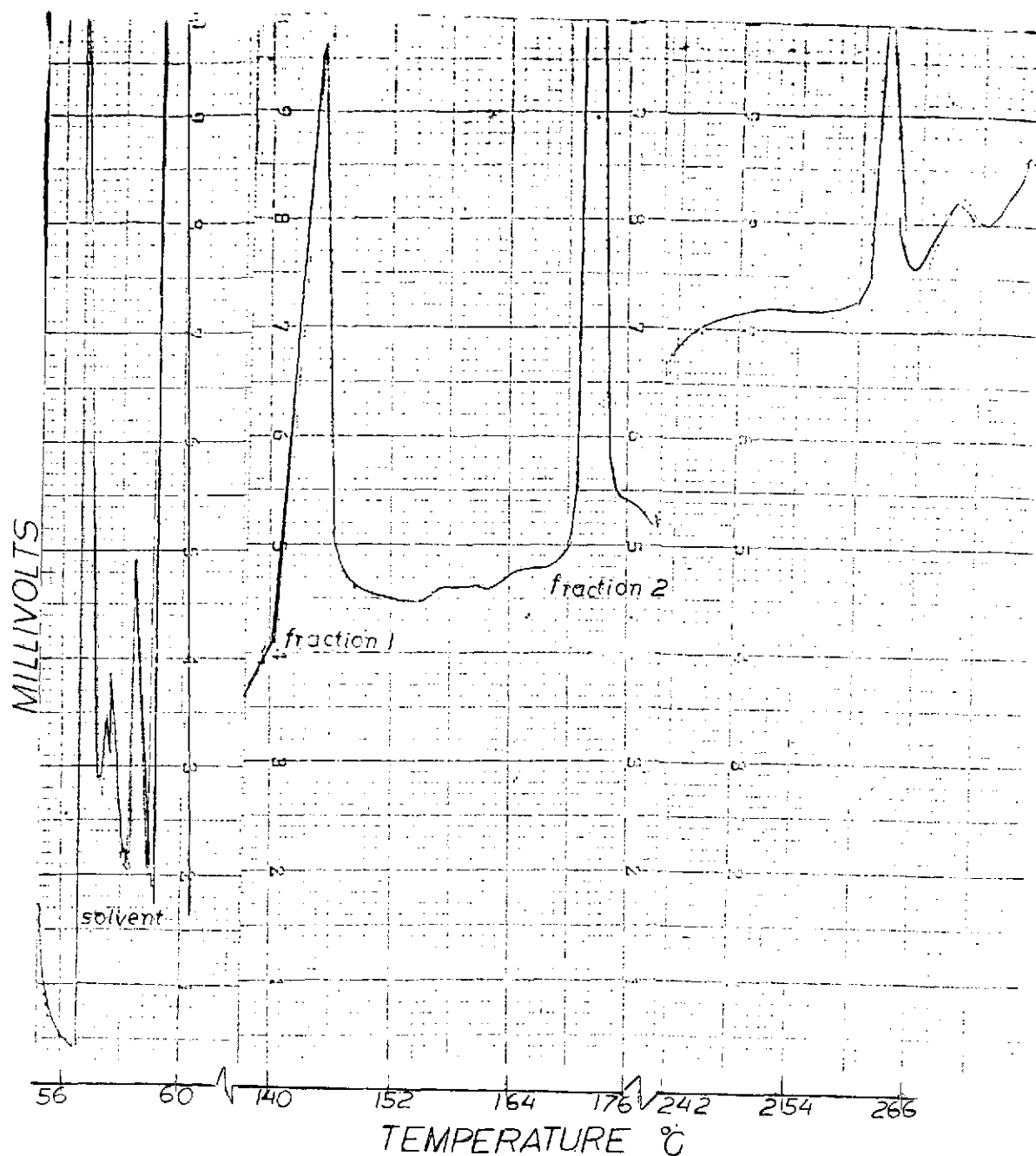


Figure 47. Gas Chromatogram of Hydrolysis Product of 1-[p-(1'-phenyl-1'-oxo-2'-oximinoethyl)phenyl]-1,2-propanedione-2-oxime.

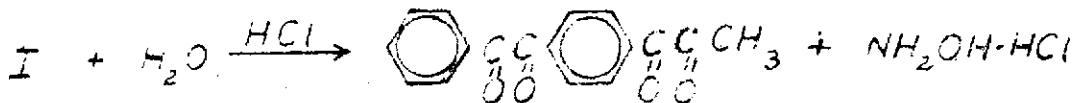
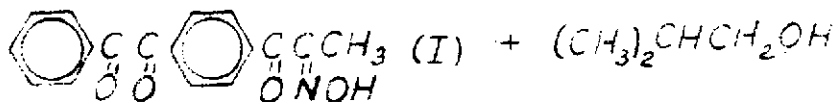
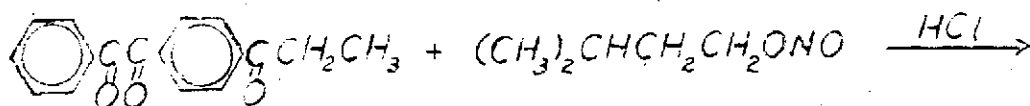
In a third attempt at ferric chloride-acid hydrolysis, 1-propanol was used as the solvent using a similar procedure. A gas chromatogram of the reaction product showed neither of the low boiling fractions shown in Figure 47.

(b) Potassium Permanganate

A solution of 2.0032 g (0.0065 mole) 1206-112-1 in 15 ml 25% NaOH was heated to 60°C and poured into 2.04 g (0.0129 mole) KMnO_4 in 35 ml water. The solution turned from a violet to a dark green color, and then a dark brown precipitate formed. The precipitate was filtered off, washed with 10 ml water and the combined washings and filtrate was acidified with dilute sulfuric acid. A white precipitate (1206-133-5) formed which was filtered off, washed with water and dried; it melted at 250- > 300°C.

3. By Hydrolysis of p-(2-Oximinopropionyl)benzil

Another possible method for preparing p-(methyloxalyl)benzil involves preparing the isonitroso derivative of p-propionylbenzil (obtained by the selenium dioxide oxidation of p-phenacylpropio-phenone as described part 1 of Appendix 3) and hydrolyzing the compound.



a. Preparation of p-(2-Oximinopropionyl)benzil

A solution of 1 g (0.0085 mole) isoamyl nitrite in 15 ml methylene chloride was added dropwise to a solution of 1.8 g (0.0068 mole) p-propionylbenzil in 35 ml methylene chloride while a slow stream of dry hydrogen chloride was passed in. After the addition was completed, the solution was refluxed for 1 1/2 hours. The reaction solution was evaporated to dryness leaving an oil (1206-121-1) weighing 2.4 g. A 1.9 g sample of the oil was crystallized from a solution of equal volumes of carbon tetrachloride and hexane. The yield of the product (1206-121-4) was 0.6 g and it melted at 114-115°C. Portions of its infrared spectrum are shown in Figure 48 and are compared with corresponding portions of the spectrum of the model compound, 1-phenyl-1,2-propanedione-2-oxime. Both compounds show absorption at 3250 and 3280 cm^{-1} which bands, according to N. B. Colthup's Spectra-Structure Correlations⁴⁴ are attributable to NH and OH stretch. The model compound absorbs at 1650 and 1660 cm^{-1} while 1206-121-4 absorbs at 1640, 1670 and 1690 cm^{-1} . In Colthup's correlations, the region 1640-1850 cm^{-1} is attributable to C=O and 1580-1700 to C=N. These observations are consistent with an assignment of p-(2-oximinopropionyl)benzil as the structure for compound 1206-121-4.

b. Attempted Hydrolysis to p-(Methyloxalyl)benzil

A solution of 0.1 g 1206-121-4 in 1 ml methyl isobutyl ketone was treated with 5 ml 5% sulfuric acid and 0.7 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The mixture was refluxed for 15 minutes, cooled and the phases were separated. The solvents were evaporated from the organic phase leaving a brown residue which was crystallized from 8 ml 50% aqueous ethanol yielding a yellow powder (1206-126-1) which slowly darkened when heated beginning at 100°C and became black when it began to melt at 226°C. Since the melting point of this compound is higher than the melting point of p-(methyloxalyl)benzil (Section IIIA 2 b), 1206-126-1 is not p-(methyloxalyl)benzil.

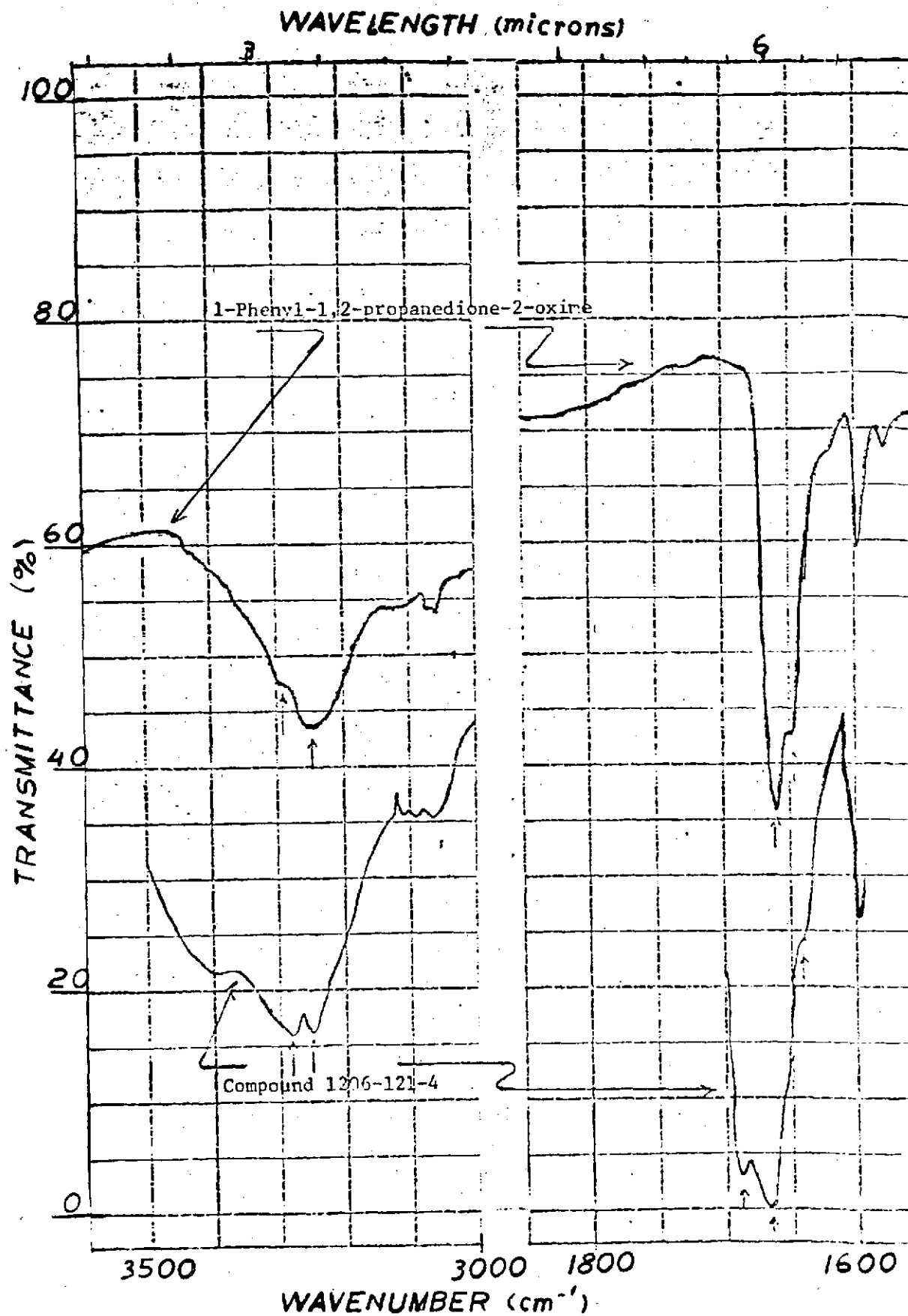


Figure 48. Comparison of Infrared Spectra of 1-Phenyl-1,2-propanedione-2-oxime and Compound 1206-121-4, Believed to Be p-(2-Oximino-propionyl)benzil.

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